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THE *CONNECTICUT* *Hard Rubber Co.*

407 EAST STREET · NEW HAVEN 9 · CONNECTICUT

September 23, 1953

Office of The Quartermaster General
Research and Development Branch
Washington 25, D. C.

Attention: Chief
Research and Development Branch

Reference: Final Report - Contract DA-44-109-QM-64

Gentlemen:

This final report contains the pertinent information obtained in the research and development work done to so formulate and process silicone rubbers that the resultant compositions be acceptable as general purpose rubbers suitable for application throughout the temperature range of -100°F to +400°F.

The assignment was successfully accomplished. The laboratory results were translated into manufactured end items suitable for application evaluation. The processes developed and the materials employed are industrially available.

Additional experimental work reported has indicated a possible method for substantial improvement of the fuel resistance of the silicone rubbers, and the studies performed on molecular cross linking point the way to improved heat resistance for them.

Very truly yours,

THE CONNECTICUT HARD RUBBER CO.


C. M. Doede
Vice President

CMD:ldj

THE CONNECTICUT HARD RUBBER COMPANY, NEW HAVEN, CONNECTICUT

DEVELOPMENT OF SILICONE RUBBERS
FOR USE AT TEMPERATURES DOWN TO -100°F

U. S. Government Contract W-44-109-QM-2161
U. S. Government Contract DA-44-109-QM-64

Project No. 7-93-15-004

FINAL REPORT
September 1, 1953

THE CONNECTICUT HARD RUBBER COMPANY, NEW HAVEN, CONNECTICUT

DEVELOPMENT OF SILICONE RUBBERS
FOR USE AT TEMPERATURES DOWN TO -100°F.

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September 1, 1953

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SUMMARY

1. An extensive study of the reinforcing action of all types of finely divided fillers in dimethyl siloxane rubbers has been made.
2. The most reinforcement was obtained with silica or alumina fillers of 0.01 to 0.02 micron diameter.
3. Maximum tensile strength of the rubber was achieved through the use of Alon, a finely divided aluminum oxide, and GS199S, hydrophobic silica, both of which affect the chemical cross-linking reaction in addition to producing reinforcement.
4. Cross-linking agents were studied but none was found to be more effective than benzoyl peroxide.
5. The cross-linking reaction was studied and it was found that:
 - (a) The cross-linking is a complicated reaction in which only 5 to 25 percent of the cross-linking occurs as a direct oxidation of methyl side chains on adjacent atoms;
 - (b) Cross-linking and substitution on the methyl groups appear to go on simultaneously;
 - (c) Cross-linking efficiency is greatest with the first 2 percent of peroxide . At higher concentrations, cross-linking efficiency is reduced.

(d) Compression set resistance is best with short, low-temperature press cures and long, high-temperature oven cures. There is no advantage in using press conditions that will be more severe than 15 minutes at 210°F.;

(e) Cross-links may be formed by the (presumed) action of atmospheric oxygen on the organic coating on hydrophobic silica in the absence of added peroxides. This action is difficult to control above 300°F.;

(f) And further study of the vulcanization of silicone rubber should be undertaken.

6. For maximum reinforcing action, fillers should be dry, and their surfaces approximately neutral. Very acid or very alkaline surfaces apparently have an adverse reaction on the rubber at the filler-rubber interface.

7. One method of promoting improved reinforcement consists in heating the filler-rubber mixture before adding the benzoyl peroxide.

8. A second method of improving reinforcement in certain cases is to depolymerize the rubber with acids, disperse the filler (with the aid of solvents) in the liquefied rubber, remove the solvents and regenerate the rubber by heating.

9. The depolymerization of silicone rubber has been studied.

One use of depolymerized silicone rubber has been worked out in the discovery that improved flex life results when glass cloth is precoated with a stabilized depolymerized rubber before being finally coated with silicone rubber compounds.

10. Depolymerized silicone rubber has been utilized as a raw material with which to react other organic molecules.

11. More extensive depolymerization occurs if the reaction is carried out in the presence of acetic anhydride and an acid catalyst.

12. Acid depolymerization affects cured gums and may have some future value in a reclaiming process.

13. The use of depolymerized gum or the use of low molecular weight silicone oils as coatings for silica aerogel fillers appears to offer promise as a way of softening the bond between silica and rubber. Further study is indicated by these results.

14. Lower molecular weight silicone rubbers result in softer compounds whose tensile strength is not greatly affected when Santocel C, silica aerogel, is used with benzoyl peroxide as the curing agent. Higher molecular weight gums are difficult to load with filler. With GS199S hydrophobic silica, the lowest molecular weight gum samples result in low tensile strengths without much change in hardness. Tensile strength measurements above 1500 p.s.i.

resulted when higher molecular weight gums, which would ordinarily be considered too tough, were used.

15. GS199S hydrophobic silica compounds may be made with concentrations as high as 50 volumes of filler to 100 volumes of gum. The best tensile strengths are obtained with concentrations between 15 and 25. Rate of cure and rate of aging are decreased at the lower concentrations (15 volumes filler per 100 of gum). Repeated milling offsets to some extent the excessive cross-linking which occurs at curing temperatures above 300°F.

16. The cohesive energy density of silicone rubber is $7.50 \pm .05$. This was ascertained by a series of swelling experiments in which corrections were made for polymer extracted during the swelling. Approximate values of M_c , the molecular weight between cross-links, were found by using a method of approximations to arrive at the polymer-solvent interaction parameter, χ . The course of future use of the swelling technique as a tool in studying cross-linking and reinforcement has been indicated.

17. Chlorinated silicone rubber was first produced under this contract and has been studied further under another contract. The chlorinated polymer gives promise of being a useful compromise for applications of silicone rubber requiring fuel-resistance.

18. Silicone rubber adhesive tapes were first produced under this contract and led to further study under another contract. Such tapes

are useful at sub-zero temperatures and at elevated temperatures where other adhesive tapes fail.

19. Methods of improving the low physical properties of silicone rubber have been developed in this work. In certain cases, some compromise of high-temperature stability in order to achieve the high physical properties has been necessary.

INTRODUCTION

Shortly after World War II, military exercises were conducted under conditions of extreme cold. It was found as a result of these tests that practically all articles composed of rubber and rubberlike materials became hard, brittle and nonextensible at low temperatures. It was found, for example, that rubber tires could be easily shattered by a blow with a hammer, and fanbelts, coated fabrics, gaskets and seals were so hard and stiff as to be completely unusable under these conditions. As a result, the Office of the Quartermaster General undertook a research program, the object of which was to provide rubber and rubberlike materials which would maintain their functional properties over the temperature range of -65° to $+140^{\circ}\text{F}$.

The silicone rubbers were selected for intensive investigation because of the fact that silicone rubbers retain their resiliency over the wide temperature range of -100° to $+400^{\circ}\text{F}$. This unique property of the silicone rubbers has not been duplicated in any other elastomeric material. At the time that the program was started, however, the best commercially available silicone rubbers suffered from low strength, poor abrasion-resistance and properties which were inferior generally to those of other elastomeric materials. Investigation to improve the

physical properties of silicone rubber was an obvious line of attack to provide a more generally useful low-temperature and high-temperature rubber.

The original approach to the problem was to ascertain whether or not it would be possible to reinforce silicone rubbers in much the same manner as is used with carbon black in the reinforcement of natural and synthetic rubbers. It was thought, for example, that if some means could be found, either by compounding or by chemical modification, to achieve improvement in silicone rubbers by reinforcement, as is done when carbon black is added to other rubbers, silicone rubbers could be used for many more military applications. It was thought desirable, too, that this reinforcement should be obtained without sacrifice of the high- and low-temperature properties inherent in silicone rubber.

Two successive contracts were entered into by the Office of The Quartermaster General to achieve these ends. They were "Development of Silicone Rubbers for Use at Temperatures down to -100°F.", U.S. Government Contract W44-109-qm-2161 (Final Report submitted March 1, 1950); and DA44-109-qm-64, of the same title, of which this is the final report, (submitted September 1, 1953). The specific assignments made under Contract W44-109-qm-2161 and under Contract DA44-109-qm-64 and in the subsequent

amendments are given at the close of this Introduction. Since the objectives of the two contracts were broadly the same, the present report can be considered a summary of both. For the convenience of the reader who may wish to refer to earlier progress reports for details, the following table of references is given:

<u>Contract No.</u>	<u>Date Submitted</u>	<u>Report Referred to Herein as</u> _____
W44-109-qm-2161	7/15/49	1
"	3/1/50	2
DA44-109-qm-64	5/1/50	3
"	8/25/50	4
"	12/11/50	5
"	4/10/51	6
"	3/28/51	7
"	9/28/51	8
"	1/15/52	9
"	5/8/52	10
"	6/5/52	11
"	11/18/52	12
"	3/13/53	13
"	9/1/53	14 This Report

At the beginning of the studies under Contract W44-109-qm-2161 and also under Contract DA44-109-qm-64 in late 1948 and 1949 respectively, it was logically decided that the greatly needed reinforcement of silicone rubber should be sought by finding the effects of

1. Particle size
2. Particle shape
3. Particle surface
 - a. Extent of surface
 - b. Nature of surface

4. Nature of the rubber-pigment bond

These variables have been kept in mind throughout the work, even though this original scope was greatly broadened as promising leads developed. After the first year of work, during which a systematic investigation of the above factors was carried out, it appeared advisable to supplement this mode of attack with an Edisonian approach in which any and all feasible reinforcing agents for silicone rubber were given at least cursory testing. This approach, being moderately successful, has been followed throughout the course of the work, and has perhaps met with greater success than the systematic unraveling of the mysteries of reinforcement. These cannot yet be clearly defined or explained. There is today (1953) a much greater possibility of their being solved than there was in 1948 or 1949 because of the greater knowledge of the polymer itself, of the degree of reinforcement possible with various pigments, of the improved methods for studying reinforcement such as by swelling studies, and also because more uniform, clean polymer is readily available in a variety of molecular-weight ranges.

Since silicone rubber contains no complicating double bonds and practically no impurities and since it can be vulcanized with a small amount of a single agent, it is the ideal system for studying both reinforcement and vul-

ization. In this work, vulcanization with benzoyl peroxide has been investigated by swelling studies in the absence of complications by reinforcing agents. It has only recently occurred to us that it should be possible to study reinforcement without the complications of vulcanization by examining the properties of silicone rubber compounded with DuPont Hydrophobic Silica, by using only sufficient heat and pressure to form test pieces. This silica possesses the property of vulcanizing as well as reinforcing silicone rubber, but the vulcanizing property can be minimized by pressing at temperatures below 300°F.

When the work was started, the only raw polymer available on the market was General Electric's 9979G (later called SE-79). About seventy-five different pigments were tried as reinforcing agents in this rubber. Early in 1951, General Electric made available their 81176 or SE-76 rubber. The ease of compounding and superior test values obtained with this gum made it advisable to change at once to this product for reinforcement studies. In general, pigments which reinforced SE-79 also reinforced SE-76, so little duplication was necessary. All newer pigments have been tested in the newer rubber. SE-76 is more comparable to most other elastomers in that it is soluble in solvents and is not cross-linked appreciably. In this respect, it differs from SE-79 which cannot be

dissolved unless depolymerized with acids. The greater degree of similarity of SE-76 to other types of rubber, and the better results obtained with it, probably make the most recent portion of the contractual work of greater value than that carried out on the cross-linked SE-79 which appears to be superseded by the non-cross-linked types.

ASSIGNMENTS

1. Conduct a series of fundamental studies on the reinforcement of rubber by the treatment of currently available rubber carbon blacks and other reinforcing pigments to make them compatible with silicone-type polymers.
2. The selection and development of a catalytic condensing composition that will work on the pigment-reinforced system referred to in (1) above.
3. Modification of the fundamental characteristics of the present polymer so as to produce greater chain length and the modified cross-linkages necessary for greater strength.

Taken from Modification "C" of Contract DA44-109-qm-64,
dated October 4, 1950

4. Pursue new developments on the liquefaction of silicone rubbers by the use of anhydrous acids and their repolymerization after adding fillers.
5. Obtain improved polymers of silicone, particularly by the utilization of the hydrolysis of the alkyl-chlorosilanes with a combination of water and alcohols of various types.
6. Study new methods of cross-linking to produce better silicone polymers.

7. Continue the study, development and test of methods to improve the reinforcement of silicone rubber and the polymer itself to obtain desired low-temperature characteristics.

Taken from Modification "E" of Contract DA44-109-qm-64,
dated September 21, 1951

8. Study extensively methods of silicone vulcanization, including types of vulcanizing agents. Vulcanizing agents other than PbO_2 should be investigated.
9. Investigate, in detail, surface effects of pigments, with particular emphasis on pH relation to physical properties.
10. Introduce reactive groups at high temperatures in air and in the presence of chemical oxidizers such as chromates, permanganates, etc.
11. Follow any practical and special applications which show promise, growing out of the contract, at least to the point of proving whether they are of value or not.

TABLE I (cont.)

<u>Name</u>	<u>Composition</u>	<u>Supplier</u>	<u>Specific gravity</u>	<u>Surface area, sq. m. per g.</u>	<u>Particle size, microns</u>	<u>pH</u>
Silene EF	Hydrated ppt'd. calcium silicate	Columbia Chemical Div.	2.1		0.25	10.0
Crown clay	Kaolin	E. Jacoby	2.6			
Monastral	Phthalocyanine	duPont	1.26			
Blue CP						
Kel-F	Polymer -OF ₂ -CHF-	M. W. Kellogg	2.2			

TABLE I (cont.)

<u>Name</u>	<u>Composition</u>	<u>Supplier</u>	<u>Specific Surface area, Particle gravity sq.m.per g.</u>	<u>size microns</u>	<u>pH</u>
Micronex W6	EPC Black	Binney and Smith	1.8	91.5	0.03
Silica 1240	Silica	Innes Speiden	4.2		5-10
Titanox RANC	94% Rutile TiO ₂ plus Al ₂ O ₃ , SiO ₂ , ZnO	Titanium Pigment			0.35
Hydrate Al	Hydrated alumina				
C741					
Dicalite No. 1	Uncalcined diato- maceous earth	Dicalite Div.	2.0	20.3	2-10
Linde Silica	Silica	Linde Air Prod.			
Titanox RC	30% Rutile TiO ₂ 70% Ca SO ₄	Titanium Pigment	3.25		0.65
Witcarb R	Ppt'd. CaCO ₃	Witco Chem.	2.65	32	0.05
Lithopone	30% ZnS 70% BaSO ₄		4.2		11.3
Michigan No. 30	Light Calcined magnesium oxide	Michigan Chemical			
Mapico 297	Comm. pure iron oxide	Binney and Smith	5.17		0.35
Fume Silica	Silica XC54	duPont	2.2		0.01 - 0.03
TiPure 510	Rutile TiO ₂	duPont	4.2		
Magnesium carbonate			2.2		
Atomite					
Barium sul- fate	Ground CaCO ₃	Thompson-Meinman	2.71		2.05
Al Flake 5	Aluminum flake		4.3		
Al Flake Fine	" "	Aluminum Flake Co.	2.65		
	" "	" "	2.65		

TABLE I
Properties of Pigments Tested
(arranged in same order as Table II)

<u>Name</u>	<u>Composition</u>	<u>Supplier</u>	<u>Specific gravity</u>	<u>Surface area, sq.m.per g.</u>	<u>Particle size, microns</u>	<u>pH</u>
Alon	Aluminum oxide	G. L. Cabot	3.6	60	0.03	
Celite 505	Calcined diatomaceous earth	Johns-Manville	2.15		1-6	7.5
Hi-Sil	Silica	Columbia Chem. Div., Pittsburgh Plate Glass	1.95		0.025	
AZO-ZZZ-55	Zinc Oxide (American process Pb-free)	American Zinc Sales	5.6		0.2	
Protox 166	Zinc oxide(Amer. process with propionic acid)	N. J. Zinc	5.57	2.4	0.35	
Dicalite White	Flux-calcined diatomaceous earth	Dicalite Div.	2.33	9.5	2-6	
Linde Silica 30	Siloxane-coated silica	Linde Air Prod.	-	-	-	
Celite 322	Flux-calcined diatomaceous earth	Johns-Manville				
Dicalite PS	Calcined diatomaceous earth	Dicalite Div.	2.25	3.2	2-6	7.5
Super Multi-flex	Coated ppt'd. CaCO ₃	Diamond Alkali	2.65		0.035	
Rayox 110	Rutile TiO ₂	R.T. Vanderbilt	4.2			

CONTRACT W44-102-gm-2161Reinforcement of SE-79

The program which was followed under the above contract has been given on page 3 of the Introduction of this report. As pointed out there, approximately seventy-five different pigments were tried as reinforcing agents for the only silicone rubber commercially available at that time, known as General Electric Silicone Rubber 9979G. This is now called SE-79.

When SE-79 is received, it is a crumbly, facticelike material. It is evidently partially cross-linked, which accounts for its crumbly nature. SE-79 is a polymer of dimethyldichlorosilane which is first hydrolyzed to produce the silanol which immediately condenses to form linear or cyclic liquid polymers. Under the influence of catalysts, these liquid polymers are then condensed further to form the rubber. Traces of the monomethyltrichlorosilane, if present, tend to result in three-dimensional or cross-linked polymers, and traces of trimethylmonochlorosilane, if present, function as chain stoppers. By varying the amounts of these mono- and tri-functional ingredients, the characteristics of the dimethyl silicone rubber may be varied. In the case of SE-79, it is understood that the catalyst used is hydrated ferric chloride, and the polymer contains traces of iron.

When placed on the mill, SE-79 smooths out in approximately the same manner as factice. If benzoyl peroxide is added and the compound cured, it assumes the form of the mold, but it is found that physical tests are very low--approximately 10 p.s.i. tensile strength and 100 percent elongation. Silicone rubber is an extreme example of a synthetic rubber which requires reinforcement.

The basic recipe established at this time consisted of 100 parts of General Electric Silicone Gum SE-79 and two parts of Luperco AS (95% benzoyl peroxide coated with stearic acid). It had also been decided that 25 parts of filler by volume was a desirable standard loading to be tried first with all fillers. In some of the earliest work, one part of lead oxide was included as a curing aid. This was soon discontinued on the advice of General Electric chemists, since it apparently served no useful purpose.

The mixing procedure was as follows:

Twenty-five grams of rubber was placed on cold, tightly set rolls of a 6" x 12" Thropp laboratory mill. The front roll rotated at the rate of 16 r.p.m. and the back roll at 23 r.p.m. (With the start of compounding of SE-76 in 1951, roll speeds were increased to 36 and 44 r.p.m.) As soon as the rubber had smoothed out on the rolls, the filler was added gradually until it was all

incorporated and then the benzoyl peroxide was added. This tight milling or refining was then continued until a small ball of stock could be formed in the fingers without showing laminations.

Compounds were next cured in a press at 220°F. for 15 minutes, the mold being cold when placed in the press and cooled to room temperature before removal. An oven curing cycle starting at room temperature and reaching 410°F. at the end of 42 hours was adopted. A gradually rising temperature tends to eliminate blowing or blistering which may occur if the temperature is raised too rapidly, especially in the presence of low-molecular-weight rubber or silicone oils or in the presence of high percentages of benzoyl peroxide. It is common practice in the industry to raise oven curing temperatures slowly if the part being cured has a thickness of more than approximately 1/8 inch.

A recipe consisting of 100 parts of SE-79 gum, 75 parts of titanium dioxide and 100 parts of Celite 505 plus 2 percent benzoyl peroxide gave the following tests on three successive batches.

<u>Tensile</u>	<u>Elongation</u>	<u>Hardness</u>
486	100	70
475	100	67
450	87.5	68

TABLE II (cont.)

<u>Pigment</u>	<u>Compound Number</u>	<u>Gram pigment per 100g. gum</u>	<u>Total Surface sq. m./100g. gum</u>	<u>Hardness</u>	<u>Tensile</u>	<u>Elong.</u>	<u>Tensile Product</u>
Titanox RANC	1123	114.1		40	114	150	171
Hydrate Al C741	1156			36	103	162½	167
Dicalite No. 1	1103	54.4	1104	40	119	125	149
Linde Silica	1125			67	214	67½	134
Titanox RC	1122	89.1		30	73	175	128
Witcarb R	1107	72.0		30	63	200	126
Lithopone	1106	114.1		25	38	287½	109
Michigan No. 30	1110			32	62	175	107½
Mapico 297	1100	140.3		35	85	157½	107
Fume Silica	1120	59.8		37	86	125	107
				36	95	150	143
Dupont TiPure 510	1119	114.1		36	64	162½	104
Mg Carbonate	1111	59.8		30	52	175	91
Atomite	1109	73.6		40	66	112½	77
Barium Sulfate	1113	116.9		31	51	150	77
Al Flake 5	1154	66.2		67	31	50	16
Al Flake Fine	1155	63.2		71	90	250	224
Silene EF	1099	57.1		No cure	-	-	-
Crown Clay	1114	70.6		No cure	-	-	-
Monastral Blue CF	1124	34.2		No cure	-	-	-
Kel-F	1207	57.5		30	0	87½	0

TABLE II

STUDIES OF PIGMENTS, AS RECEIVED, AT 25-VOLUME LOADING

Pigment	Compound Number	Gram pigment per 100g. gum.	Total Surface sq.m./100g. gum.	Hardness	Tensile	Elong.	Tensile Product
Alon	1121	97.8	5868	50	308	300	924
				64	397	212	840
				60	245	137½	347
				45	289	162½	470
Celite 505	1072	58.4		50	298	125	370
				47	267	137½	368
				46	250	137½	344
				40	158	125	197
				62	240	125	300
Hi-Sil	1073	53.0		62	193	112½	227
				54	182	100	182
				33	151	187½	283
AZO-ZZZ-55	1101	152.2		39	88	125	110
				37	126	212	267
Protox 166	1102	151.4	363	32	95	287½	263
				36	140	162½	227
Dicalite White	1105	63.3	146	60	243	87½	212
Linde Silica 30	1098			39	144	137½	198
Celite 322	1091			40	133	150	199
Dicalite PS	1104	61.1	196	34	95	200	190
Super Multiflex	1108	72.0		35	89	200	178
Rayox 110	1118	114.1		47	175	100	175
Micronex W6	1093	48.9	4480	No cure			
				37	105	162½	171
Silica 1240	1071			32	89	175	156
				37	93	150	139

In the final report on the first contract, data were reported on some thirty fillers which had been tried in SE-79 rubber. Table I gives the name of the pigment, its manufacturer and physical data supplied by the manufacturer of the pigment. A wide variety of pigments was included.

Table II shows the results obtained with these pigments at a volume loading of 25 volumes of pigment per hundred of rubber. One of the smallest particle size fillers tried at this time was Alon, and it was found that tensile strengths as high as 400 p.s.i. and an elongation of 212 percent could be obtained with this material. Alon, about which more will be said later in the report, was definitely an experimental product of the G. L. Cabot Company and was at that time, and still is, very expensive. A more common and economical material, Celite 505, also appeared of interest. It is a much coarser product than Alon and is a ground, calcined, diatomaceous earth. It is widely used in silicone rubber compounding, probably because it can be used in large quantities without creating excessive hardness. Part of its value undoubtedly lies in the fact that it is porous and forms a good mechanical bond with the rubber.

It is of interest to note that a very fine carbon black, Micronex W6, gave results which were definitely inferior to those obtained with Alon.

TABLE III
STUDIES OF PIGMENTS, AS-RECEIVED, AT VARIABLE LOADING

Pigment	Compound Number	Volumes Pigment Per 100 Vol. Gum	Weight Pigment Per 100 Wt. Gum	Hard-ness	Ten-sile	Elonga-tion
Celite 505	1165	10	23	25	63	150
	1166	20	47	35	81	137½
	1072	25	57	45	289	162½
		25	57	50	298	125
		25	57	47	267	137½
		25	57	46	250	137½
		25	57	40	158	125
	1167	30	69	35	169	150
	1168	40	93	45	205	112½
	1196	43	100	57	405	100
	1070	65	150	78	505	75
	1169	65	150	69	550	75
	1204	2.6	10.4	21	25	200
	1205	4.0	15.6	25	26	175
	1206	5.3	21.0	28	48	175
Alon	1160	10.0	39.2	30	112	200
	1161	30.0	78.5	52	228	162½
	1121	25.0	97.5	50	308	300
	1195	25.0	97.5	64	397	212
	1162	25.0	97.5	60	245	137½
	1195	25.5	100	No Cure	-	-
	1162	30.0	117	87	332	50
	1163	40.0	157	No Cure	-	-
	Dicalite 1090	25	61	40	133	150
	PS 1057	41	100	59	428	100
Hi-Sil	1171	61	150	69	291	72½
	1172	10	21.4	24	58	275
	1173	20	42.8	44	145	150
	1073	25	53.5	62	240	125
		25	53.5	62	193	112½
		25	53.5	54	182	100
	1174	30	64.2	61	145	75
Silica 1240	1175	40	85.6	No Cure	-	-
	1071	25	67	37	105	162½
		25	67	37	93	150
		25	67	32	89	175
AZO-ZZZ-55	1170	56	150	50	216	100
	1061	16.4	100	32	144	225
	1101	25	152	38	151	187½
		25	152	39	88	125
Protox X-166	1062	16.7	100	28	184	512½
	1102	25	151	37	126	212
		25	151	32	95	287½

Some of the fillers which gave the highest results in Table II were compounded further at several volume loadings (Table III). In this way, it was found that Celite, for example, could be used to obtain 550 p.s.i. tensile strength at a volume loading of 65. Except for Alon, as mentioned above, none of the other fillers appeared to be as useful as Celite 505.

Modification of Surface of Fillers

Investigation of the nature of the particle surface was the next part of the program that was studied. It was suggested by Mr. Peter King of the Naval Research Laboratories that we do a thorough job of heat-cleaning the surface of some of the pigments in order to remove volatile or adsorbed gases from the surface of the filler. In order to do this, arrangements were made to heat and apply vacuum to the fillers. The various treatments used are listed below.

1. Heating to 400°C. in air
2. Heating to 1000°C. at .0001 mm. pressure
3. Heating to 400°C., allowing to cool in air, then admitting dimethyldichlorosilane vapor, followed by admitting water vapor to form a silicone coating
4. Heating to 1000°C. and coating, as above
5. Heating to 400°C., followed by coating with a silicone oil

6. Heating to 400°C. and coating with another silicone oil
7. Applying benzoyl peroxide, dissolved in benzene, to filler

With treatments (1) and (2), it was hoped to remove tightly held water or other foreign substances from the pigment surface. Treatments (3) and (4) were designed to deposit a siloxane coating on the filler. This was done by causing the hydrolysis of dimethyldichlorosilane to occur on the surface of the filler. Treatments (5) and (6) were carried out to coat the out-gassed fillers with two different silicone oils. Work reported later in this report shows that the addition of silicone oils to the surface of porous fillers does have an effect on the physical tests obtained. Such was not the case in this early work. Treatment (7) was designed to promote a tighter (cured) bond at the pigment-rubber interface. Significant improvement in tensile strength resulting from out-gassing or from out-gassing plus addition of coatings did not result from this work. The fillers that were treated were Micronex W6, Silica 1240, Celite 505 and Hi-Sil. These data are not reproduced here but may be found in the Final Progress Report on Contract W44-109-qm-2161, dated March 1, 1950.

TABLE IV (cont.)

STUDIES OF PIGMENTS, AS RECEIVED, AT 25-VOLUME LOADING

Name	Composition	Average Particle Size, Microns	Tensile Strength (p.s.i.)	Elongation (Percent)	Hardness (Shore A)
Super Multiflex	Coated precipitated calcium carbonate	0.035	95	200	34
Ti Pure 510	Rutile titanium dioxide		65	165	36
Titanox RAC	94% Rutile titanium dioxide plus alumina oxide, silicone dioxide, zinc oxide	0.35	115	150	40
Titanox RC	30% Rutile titanium dioxide 70% calcium sulfate	0.65	75	175	30
Witcarb R	Precipitated calcium carbonate	0.05	65	200	30

NOTE:

The particle size was taken from manufacturer's information
Tensile strength, elongation and hardness values are the average of those obtained
by testing three dumbbells from each of two slabs.

TABLE IV (cont.)

STUDIES OF PIGMENTS, AS RECEIVED, AT 25-VOLUME LOADING

Name	Composition	Average Particle Size, Microns	Tensile Strength (p.s.i.)	Elongation (Percent)	Hardness (Shore A)
Mapico Black	Iron oxide	0.2	140	120	43
Mapico Brown 418	Iron oxide		220	160	43
Mapico Crimson 88	Iron oxide	0.2 - 0.6	235	145	44
Mapico Red 297	Commercial pure iron oxide	0.35	85	160	35
Mapico Red 347	99.3% ferric oxide	0.06	150	115	48
Mapico Red 387	99.3% ferric oxide	0.06	85	120	35
Mapico Tan 20	Iron oxide	0.1 - 0.8	175	150	46
Mapico Yellow 100	Iron oxide	0.2	190	170	40
Mapico Yellow	Iron oxide	0.1 - 0.8	160	125	41
Dark Orange					
Michigan No.30	Light calcined magnesium oxide		60	175	32
Micronex W6	EPC Black	0.03	175	100	47
Monastral Blue	Phthalocyanine		No cure		
MP-561-1	Anatase titanium dioxide	0.06 - 0.3	140	125	42
MP-561-2	Anatase titanium dioxide	0.01 - 0.12	165	150	44
IP-561-3	Anatase titanium dioxide	0.01 - 0.06	110	50	55
Prottox 166	Zinc oxide(American process with propionic acid)	0.35 -	110	250	35
Rayox 110	Rutile titanium dioxide		90	200	35
Santocel C	90% silica	3 - 5	115	55	66
Santocel CX	90% silica		285	60	68
Silene EF	Hydrated precipitated calcium silicate	0.2 - 0.3	145	155	41
Silica 1240	Silica	5 - 10	95	165	35
Statex A	CF Elack		155	130	40
Statex B	FF Black		70	100	42
Sterling L	HMF Black	0.06	No cure		

TABLE IV

STUDIES OF PIGMENTS, AS RECEIVED, AT 25-VOLUME LOADING

Name	Composition	Average Particle Size, Microns	Tensile Strength p.s.i.	Elongation (Percent)	Hardness (Shore A)
Alon	Aluminum oxide	0.03	315	215	58
Alon II	Aluminum oxide	0.005 - 1.0	140	180	34
Al Flake 5	Aluminum flake		30	50	67
Al Flake Fine	Aluminum flake		90	250	71
Atomite	Ground calcium carbonate	2.05	70	115	40
AZO-ZZZ-55	Zinc oxide(American process lead-free)	0.2	120	160	38
AZO-ZZZ-66	Zinc oxide(French process lead-free)		100	140	38
Barium sulfate			50	150	31
Celite 322	Flux-calcined diatomaceous earth		145	140	39
Celite 270	Calcined diatomaceous earth	1 - 6	250	140	43
Celite Snow Floss	Uncalcined diatomaceous earth	1 - 2	155	125	43
Celite Super Floss	Flux-calcined diatomaceous earth	2 - 4	180	125	40
Crown clay	Kaolin		No cure		
Dicalite No.1	Uncalcined diatomaceous earth	2 - 10	120	125	40
Dicalite PS	Calcined diatomaceous earth	2 - 6	135	150	40
Dicalite SA-3	Uncalcined diatomaceous earth	2 - 40	240	130	52
Dicalite UF	Calcined diatomaceous earth	2 - 40	180	150	41
Dicalite White	Flux-calcined diatomaceous earth	2 - 6	140	165	36
Fume Silica	Silica .AC54	0.01 - 0.03	90	140	37
Furnex	SNF Black		39	50	37
Hi-Sil	Silica	0.025	205	115	59
Hydrate Al C741	Hydrated alumina		100	160	36
Linde Silica	Silica		215	70	67
Linde Silica 30	Siloxane-coated silica		245	90	60
Lithopone	30% zinc sulfide, 70% barium sulfate		40	290	25
Magnesium Carbonate			50	175	30

CONTRACT DA44-109-am-64Reinforcement of SE-79

The testing of a wide variety of fillers commonly used in the rubber industry was continued under the new contract, and by the end of 1950 some fifty-five potential reinforcing agents had been tried. Table IV, taken from a paper entitled, "Reinforcement of Silicone Rubber", by Gline, Duke and Docde, summarizes all of this work.

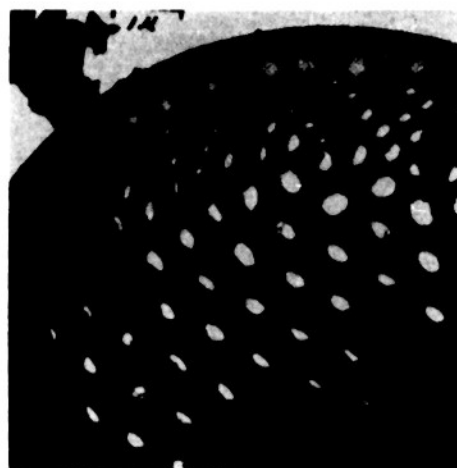
Some work was done at this time in which mixtures of fillers were tried in the hope that one filler which provided high tensile might be combined with one which imparted high elongation, to give a high elongation-high tensile result. This was not found to be the case.

Through the cooperation of Yale University Medical School, an RCA Model, EMU electron microscope was made available, and electron micrographs were taken of twenty-four of the fillers used in the program. These photomicrographs are reproduced on the following pages.

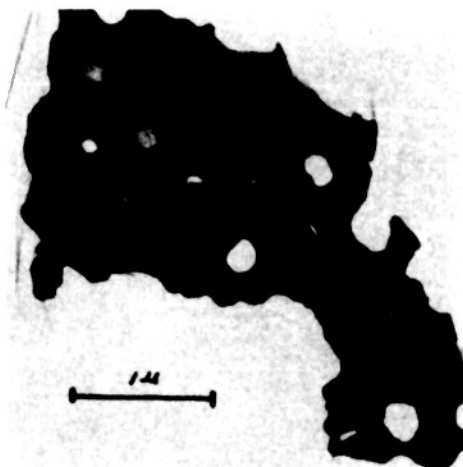
Before concluding this portion of the work, the method of mixing was reviewed. It was observed that the more strongly reinforcing pigments, such as Alon, tend to dry up the batch on the mill. If such dry batches are given only a limited milling, they will tend to be "short", and low elongation, tensile and hardness results will be



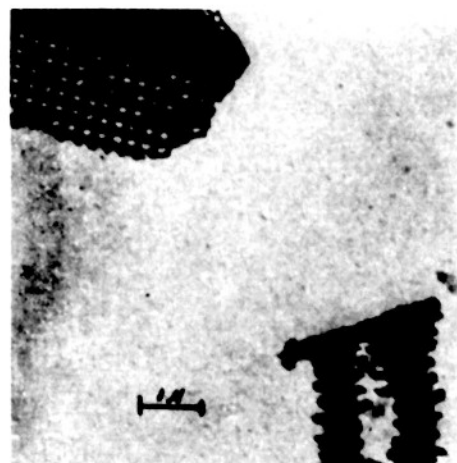
CELITE 505
9,700X



CELITE 505
8,300X



CELITE 505
19,400X



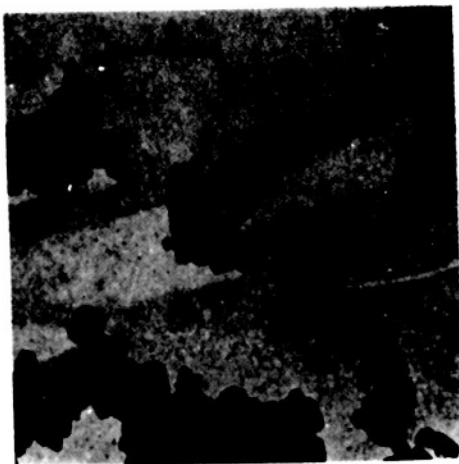
DICALITE WHITE
8,300X



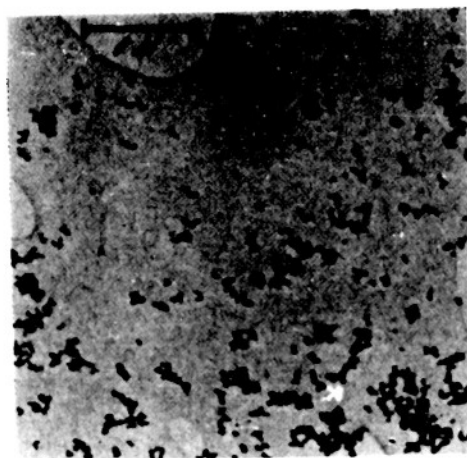
DICALITE PS
7,300X



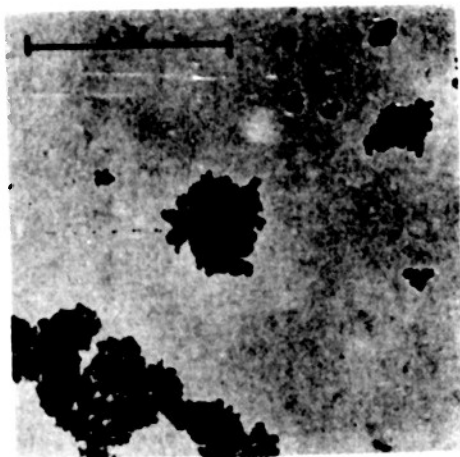
DICALITE PS
7,300X



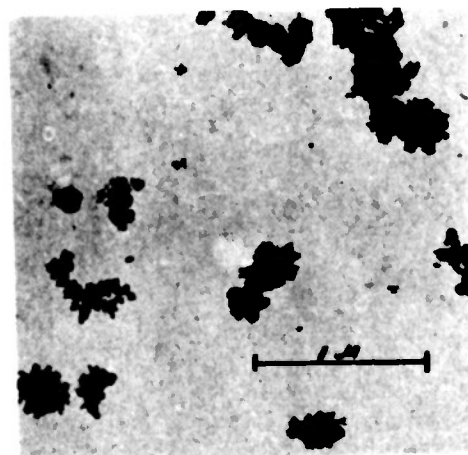
SILICA 1240
13,500X



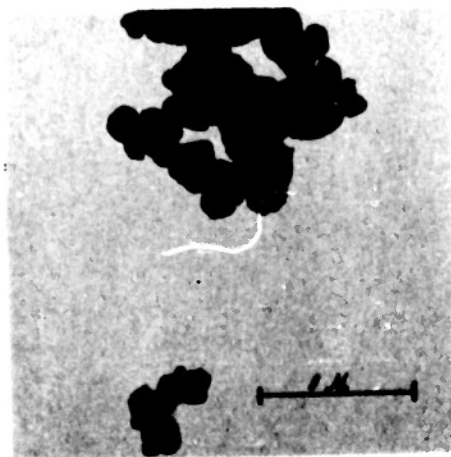
MICRONEX W-6
15,100X



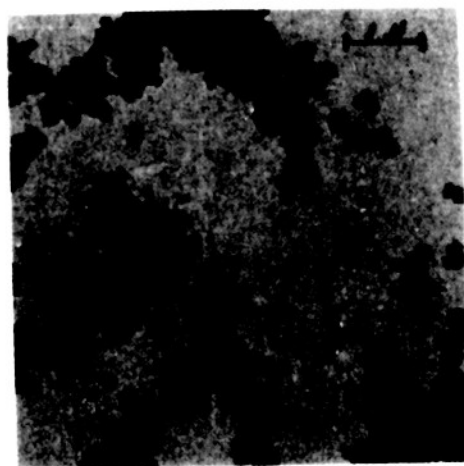
HI-SIL
26,800X



ALON
22,800X



TITANIUM DIOXIDE
21,300X



RAYOX 110
10,000X



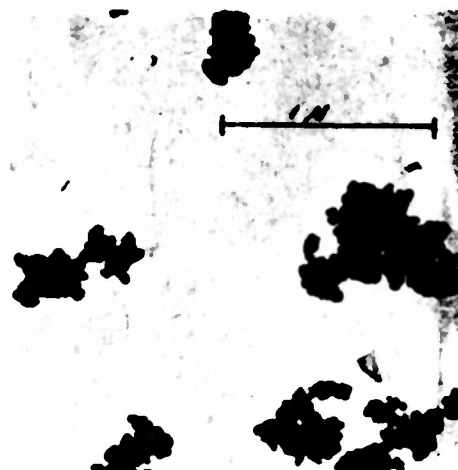
AZO-ZZZ-55
10,000X



AZO-ZZZ-55
21,300X



AZO-ZZZ-55
28,100X



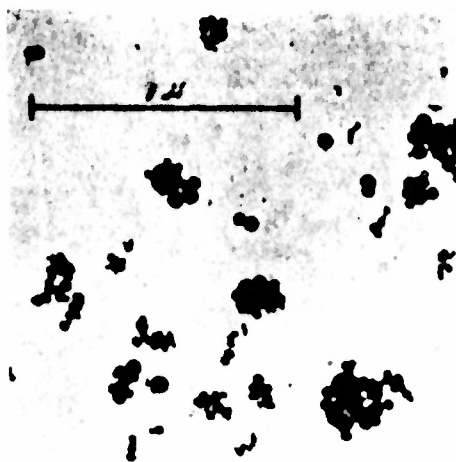
SUPER MULTIFLEX
28,100X



AZO-ZZZ-66
7,600X



AZO-ZZZ-66
10,000X



FUME SILICA
34,800X



FUME SILICA
34,800X



MAPICO TAN 20
21,300X



MAPICO TAN 20
28,100X



RANEY NICKEL
13,500X



RUFERT NICKEL
8,300X

obtained. Hence, it is necessary to mill silicone compounds until they are definitely plastic. When this is done, the maximum physical properties are obtained. As far as could be observed, prolonged milling has no detrimental effect.

Under optimum conditions of milling, 'lon and Celite 505 could be made to give tensile strengths of 400 p.s.i. with elongations of 100 to 200 percent at 25-volume loadings. Heavier loadings pushed tensiles to 500 and 600 p.s.i., but as far as JE-79 polymer was concerned, this appeared to be the limit that could be obtained by conventional mixing procedures with the fillers and curatives that are available.

Electrostatic Contact Potential Theory of Reinforcement

There is a theory of reinforcement called the Electrostatic Contact Potential Theory of Reinforcement. Considerable work has been done on this theory by Dr. R. S. Havenhill of the St. Joseph Lead Company. To test the theory in silicone rubber, nine samples containing various pigments were compounded and submitted to Dr. Havenhill for measurement of the contact potential. The data obtained showed that there was some degree of correlation between tensile strength and contact potential. Because it is felt that this work might profitably be continued, the entire section from Report No. 6 on this

subject is reproduced below. At this time, there was a change from SE-79 polymer to SE-76 polymer, and, as will appear in the following pages, improved physical tests were forthcoming immediately. Continuation of the work with Dr. Havenhill was therefore postponed, as preference was given to other aspects of the program. It is quite possible that further work with the contact potential theory, as applied to the reinforcement of silicone rubber, might provide an explanation of some of the improved reinforcement that has been obtained.

A. Contact Potential Theory

"It has long been known that rubber is electronegative relative to most substances, including the pigments commonly used as reinforcing fillers. This suggests that there may be an electrostatic force of attraction between the gum and pigment particles in a rubber compound which is important in the reinforcing action of the pigment. Dr. Havenhill and his associates at the St. Joseph Lead Company have made a detailed study of the electrostatic properties of hydrocarbon rubbers and have found provocative results to support an "Electrostatic Contact Potential Theory of Reinforcement." 2,3,4

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2. Havenhill, R.S., O'Brien, H.C., and Rankin, J.J., *Journal of Applied Physics*, 15, 731, (1944).
 3. Havenhill, R.S., O'Brien, H.C., and Rankin, J.J., *Journal of Applied Physics*, 12, 338 (1946).
 4. Havenhill, R.S., Carlson, L.E., and Rankin, J.J., *Rubber Chemistry & Technology*, 22, 477 (1949).

"If any two dissimilar substances are pressed together and then released, in general a positive (+) charge will appear on one and a negative (-) charge on the other. For example, rubber is electronegative relative to carbon black and will acquire a negative charge when separated from carbon. Havenhill, therefore, reasons that the positive carbon black should be attached to the negative rubber in a rubber compound. The positive carbon black will "neutralize" the negative rubber to produce a less negative (more positive) rubber compound, and thus the compounded rubber will become less negative as the reinforcement improves. Presumably, the most positive pigments should provide the best reinforcement. Unfortunately, Dr. Havenhill has been unable to develop a reproducible and reliable method of measuring the position of pigments in the electrostatic series, but he has developed a good method of determining the "electronegativity" of cured rubber compounds by measuring what he calls the "contact potential" of the rubber. (This term is not to be confused with "contact potential" as used in the physics of metals.)

B. Contact Potential Apparatus

"This apparatus consists of a mirror-surfaced steel plunger which can be put into contact with a cured rubber sheet and then separated from it in a reproducible way. The plunger, on separation, is positively charged and the rubber negatively charged. A special electron device

TABLE V

CURED SILICONE SHEETS (G.E. SE-79)

Compound No.	Pigment Loading 25-Vol.	Physical Test Data				Contact Potential	
		St. Joseph Lead Co.		Conn. Hard Rubber		Plunger*	Order by**
		Tensile Elong. p.s.i.	%	Tensile Elong. p.s.i.	%	Apparatus Volts per sq.in. of Surface Separation	Sheet Separation
1066	Celite 505-100 Rayox - 75	600	75	662	100	-3,250	2
1121	Alon	255	138	317	216	-1,000	1
1073	H1-Sil	200	100	205	112	-5,000	4
1072	Celite 505	195	80	252	137	-4,500	5
1102	Protox 166	195	262	110	249	-5,000	3
1123	Titanox RANC	150	100	114	150	-5,500	6
1109	Atomite	100	62	68	113	-5,300	8
1154	Al Flake 5	40	100	31	50	-6,000	9
1122	Titanox RC	40	68	73	175	-5,900	7

*Freshly cut surface .075 x 1 inch, washed with acetone and discharged with Neutrastat before and during contact.

**Freshly cut surfaces, pressed together, separated, and polarity of electrostatic charge determined. Most positive (+) charges have lowest number; most negative (-), the highest number.

measures the charge on the steel plate in terms of a voltage read on an output meter. This voltage is termed the "contact potential" of the rubber, since it is proportional to the difference in potential between the plunger and the rubber on break of contact. A large contact potential represents a very negative rubber, and, according to Havenhill's theory, a poorly reinforced one. A small contact potential, conversely, represents a less negative compound, and, presumably, a better reinforced rubber.

C. Results on Hydrocarbon Rubber

"Tensile strength is related to contact potential in natural rubber and GR-S^{2,3}. These results suggested that further study of Dr. Havenhill's ideas might be fruitful and that their application to silicone rubber reinforcement might indeed be worth investigation.

D. Results on Silicone Rubber

"Dr. Havenhill offered to cooperate with The Connecticut Hard Rubber Company in a contact potential study of silicone rubber compounds. Cured sheets of silicone rubber containing a variety of compounds were prepared at The Connecticut Hard Rubber Company and sent to the St. Joseph Lead Company for electrostatic investigation. The results of these measurements are tabulated in Table V.

"The plunger apparatus contact potential is given

for each sheet as well as the "order by sheet separation." The latter quantity was determined by measuring the sign of the charge on each of two rubber sheets, after first contacting and then separating the sheets. A series of such measurements allows the sheets to be arranged in an electrostatic series with the more negative (-) ones having the higher numbers.

E. Discussion of Results

"It is evident from the data that there is a general correlation between contact potential and tensile strength, similar to that found for hydrocarbon rubbers. The difference in tensile strength results obtained by the St. Joseph Lead Company and The Connecticut Hard Rubber Company, as well as discrepancies between contact potential and tensile results, are quite possibly due in part to poor dispersion and lack of uniformity of samples. Tests are now in progress on the improved stocks obtained by dispersing the pigment in the depolymerized gum.

"These results suggest the use of highly positive pigments as the best reinforcing fillers."

Wetting Agents

Where carbon black is a useful reinforcing agent for carbon-chain elastomers, the use of stearic acid is virtually essential to bring it to full effectiveness. A popular theory of the mechanism involved is that the

carboxyl groups of the fatty acid are strongly adsorbed by the carbon black while the long carbon chains of the acid are firmly imbedded in the hydrocarbon polymer.

Dr. C. A. Walker had suggested early in the work the possible value of making a stearic acid analogue for silicone. An intermediate molecular weight silicone ending in a carboxyl group might well be expected to improve the effectiveness of carbon black as a strengthening agent in silicone stocks.

For silica fillers, the normally present hydroxyl end groups are probably a fortunate circumstance, providing the best possible "link of attachment".

The wide variation in ease of incorporation of various fillers indicated corresponding variations in wettability. The relative ease of incorporating large amounts of Silica 1240 and many of the diatomaceous earths to give fluid, well mixed batches has always suggested the possibility of natural wetting agents being present.

All of the work on heat-cleaning and surface modification would be expected to uncover leads in this direction but it did not. The ensuing work to prepare and try a stearic acid analogue and several "stabs in the dark" for wetting agents did not uncover any obvious and profound wetting effect but the results in some cases have nevertheless been useful.

The same four pigments which were used in the outgassing experiments (page 13) were again used as fillers, together with two per cent by weight (based on the rubber) of the following wetting agents: caprylic acid, decanol-1, dodecyl ether, dodecylthioester, decyl mercaptan and Na-dodecyl sulfonate. No improvements in physical tests were observed. The only effect was a slight plasticizing action in some cases.

A first attempt at a stearic acid analogue was p-trimethylsilylbenzoic acid which was synthesized in the laboratory and tried in concentrations up to three percent (based on the rubber) in a Celite 505 and in a Celite 505-titanium dioxide recipe. Although the pigments were incorporated somewhat more easily, there was scarcely any effect on the physical tests.

Another, more empirical attempt to produce a stearic acid analogue involved hydrolyzing dimethyldichlorosilane in the presence of glycolic acid, with the hope that the glycolic acid would condense into the silicone chain, thus producing such a chain with a $-OCH_2COOH$ end group. A description of the reactions carried out is given in detail in Report No. 6. A typical one consisted in reacting dimethyldichlorosilane (one mole) with water and glycolic acid (0.1 mole). The resulting oil was condensed to form a gum by heating with potassium hydroxide. All of the

TABLE VI (cont.)

Code No.	Method of Formation	Compound No.	Parts 'A'		Tensile p.s.i.	Elongation Percent	Hardness Shore A
			Per 100	Parts Gum			
WA-9	Solid product of the reaction of silicone oil with conc. H_2SO_4	1571	1.0		142	138	38
		1572	2.0		155	113	42
	Depolymerized gum with ethylene cyanohydrin	1573	1.0		162	142	38
WA-10		1574	2.0		177	146	37
	Liquid product of the reaction of silicone oil with conc. H_2SO_4	1579	1.0		193	100	52
WA-11		1580	2.0		288	100	59
WA-12	Oxidation product of decanol and depolymerized gum. Used with stearic acid**	1581	1.0		176	200	30
		1582	2.0		164	267	34
WA-13	Oil from the reaction of depolymerized silicone gum with glycolic acid	1583	1.0		192	125	46
		1584	2.0		206	150	43
WA-15	Oil from the reaction of depolymerized gum with ethylene cyanohydrin	1585	1.0		208	138	45
	Hydrolysis of reaction product of $(\text{CH}_3)_2\text{SiCl}_2$ and ethylene cyanohydrin	1586	2.0		198	125	42
WA-16		1539	1.0		169	100	44
Average of standard batches							
Control during this period		1072	-		226	119	46

* Wetting Agent

** In addition, 0.5 parts of stearic acid were added to Compound No. 1581, and 1.0 parts to Compound No. 1582.

TABLE VI

WETTING AGENTS

Code No.	Method of Formation	Parts 1A*		Tensile p.s.i.	Elongation Percent	Hardness Shore A
		Compound No.	Per 100 Parts Gum			
WA-1	p-trimethylsilylbenzoic acid	1334	1.0	257	132	45
		1335	2.0	156	125	41
		1336	3.0	175	106	46
44-F	Gum from the hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ in water and glycolic acid	1538	5.3	168	117	43
		1536	11.1	197	125	43
		1537	25.0	183	125	44
66-B	Gum from the hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ in water and triethanolamine	1542	5.3	180	113	41
		1543	11.1	192	117	38
		1544	25.0	218	117	40
WA-2	Oil from reaction of depolymerized gum and glycerol	1556	1.0	241	179	36
		1563	2.0	327	158	44
		1597	3.0	207	129	47
WA-3	Oxidized oil from hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ in water and glycerol	1598	5.0	200	142	44
		1557	1.0	236	150	38
		1564	2.0	306	150	46
WA-4	Oil from the hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ in water and glycolic acid	1501	3.0	153	146	41
		1558	1.0	249	153	57
		1565	2.0	228	150	43
WA-5	Oil from the hydrolysis of $(\text{CH}_3)_2\text{SiCl}_2$ in water and glycerol	1559	1.0	275	150	47
		1566	2.0	235	142	43
WA-6	Oil from reaction of $(\text{CH}_3)_2\text{SiCl}_2$ with NH_3 in inert solvent	1560	1.0	196	150	38
		1567	1.0	262	142	45
		1568	2.0	223	142	44
WA-7	Gum from the hydrolysis of the reaction product of depolymerized gum with excess ethylene cyanohydrin	1569	1.0	146	142	41
		1570	2.0	188	162	33
WA-8	Gum similar to WA-7					

*Wetting Agent

various oils and gums that were produced were then tested in the SE-79 test recipe containing Celite 505, 25 volumes, and benzoyl peroxide, two percent. The products formed were, for the most part, tested in one or two percent quantities based on the gum. In two cases, as much as 25 parts of the wetting agent were used. The data obtained are shown in Table VI facing this page. This table is reproduced principally to demonstrate how gums or siloxane oils may be formed from dimethyldichlorosilane in the presence of other substances. It is apparent now that the materials should have been tested in larger proportions, possibly without SE-79. In this way, new types of rubber would have been tested. As wetting agents, none of the products tested appeared to have value.

Vulcanizing Agents

Parallel to the study of reinforcing agents, a study was made of vulcanizing agents for SE-79 rubber. Benzoyl peroxide was at that time the only recommended curing agent. It was found that there was no benefit to be derived from increasing the concentration of benzoyl peroxide above two percent, based on the rubber. This result, which was found by direct physical testing, was later confirmed in some swelling studies where the molecular weight between cross-links was measured directly.

Other curing agents were tried, including tertiary

butyl perbenzoate, ditertiary butyl peroxide, Rufert nickel, Raney nickel (nickel on kieselguhr--hydrogenation catalyst used commercially, made by the Rufert Chemical Co.), and p-trimethylsilylbenzoic acid. The nickel hydrogenation catalysts were tried because at higher temperatures they are also dehydrogenating catalysts. If they behaved in this way by dehydrogenating the methyl groups, cross-linking would result. Except for Raney nickel, all of these products acted as vulcanizing agents but all were inferior to benzoyl peroxide in development of tensile strength and elongation in the rubber.

It was known that selenium dioxide is an oxidizing agent that possesses the power to oxidize selectively the terminal methyl groups of organic compounds. It was hoped that it would oxidize the side-chain methyl groups of the silicone rubber. It was found that selenium dioxide in a concentration of two percent (based on the rubber) and in the presence of 25 volumes of Celite 505 would serve as a vulcanizing agent, resulting in a tensile strength of 184 p.s.i., an elongation of 175 percent and a hardness of 42. Further proof of the action of selenium dioxide was obtained by reacting it with a liquid silicone, hexamethyldisiloxane, at 250°C. for five hours. The oily product, when fractionated and examined by infrared spectroscopy, showed that vulcanization had occurred by

reaction of the selenium dioxide with the methyl side-chains of the siloxane. Since selenium dioxide was less effective than benzoyl peroxide, the work was not carried further.

Depolymerization of Silicone Rubber

With a view to producing finely divided pigments in situ, the thought occurred that possibly titanium tetrachloride or silicon tetrachloride might be miscible with silicone rubber and that if this were the case they could be hydrolyzed so as to form titanium dioxide and silica in a finely divided state in intimate contact with the rubber. In starting to make such mixtures of SE-79 gum with the titanium tetrachloride, it was found that 10 to 20 parts of gum could be liquefied by one part of titanium tetrachloride and it was obvious that a powerful and rapid depolymerization was taking place.

These mixtures of depolymerized rubber and pigments formed in situ could have been worked up into silicone compounds in the light of later work. Instead, attention was first turned to the liquefying reaction which changes the SE-79 gum to a liquid product. It was found that dry hydrogen chloride gas passed into a flask containing the shredded rubber would soften it gradually until it became a viscous liquid. The more gas used, the thinner the liquid, which generally was carried to a honeylike

Plate 5

Electron Micrograph of Zinc Oxide
in Silicone Rubber

Magnification 80,000 X

Compound No.1479

Composition

Depolymerized Silicone Gum	100.00
AZO-ZZZ-66 Zinc Oxide	152.00
Benzoyl Peroxide	7.80

Compounding

The HCl depolymerized silicone gum was diluted in CCl_4 and mixed with the pigment in a Waring Blendor. After repolymerizing the mixture by heating, the benzoyl peroxide was added on the mill.



ELECTRON MICROGRAPH OF ZINC OXIDE PIGMENT IN SILICONE RUBBER

80,000 X

PLATE 5

Plate 6

Electron Micrograph of Alon
in Silicone Rubber.

Magnification 80,000 X

Compound No. 1477

Composition

Depolymerized Silicone Gum	100.00
Alon	98.00
Benzoyl Peroxide	2.00

Compounding

The HCl depolymerized silicone gum was mixed with the pigment in a Waring Blendor. After repolymerizing the mixture, the benzoyl peroxide was added on the mill.



ELECTRON MICROGRAPH OF ALON PIGMENT IN SILICONE RUBBER

80,000 X

PLATE 6

Plate 7

Electron Micrograph of Hi-Sil
in Silicone Rubber

Magnification 23,000 X

Compound No.1476

Composition

Depolymerized Silicone Gum	100.00
Hi-Sil	53.50
Benzoyl Peroxide	2.20

Compounding

The HCl depolymerized silicone gum was mixed with the pigment in a Waring Blendor. After repolymerizing the mixture, the benzoyl peroxide was added on the mill.



ELECTRON MICROGRAPH OF HI-SIL PIGMENT IN SILICONE RUBBER

23,000 X

PLATE 7

consistency.

It was found that the liquid rubber could be transformed back to solid rubber simply by allowing the dissolved acid to escape, either by heating or by allowing it to stand in air. The liquid rubber was soluble in most organic solvents, which was not true of the cross-linked parent gum. The liquefied EE-79 rubber was put to several uses which will be discussed in detail below. These included: a) compounding the liquid rubber with fillers, using carbon tetrachloride to dissolve the rubber; b) reactions of the liquid rubber with ammonia, glycerine, maleic anhydride and propylene oxide; c) chlorination of the side-chains of the liquid rubber in solution; d) further reaction of the liquid rubber with acetic anhydride; and e) analysis of the liquefied rubber to determine its nature.

Experiments were also conducted with titanium tetrachloride and vulcanized silicone scrap rubber to develop a reclaiming process.

Reinforcement of Liquid Rubber

It was found that when the liquid rubber was dissolved in a solvent such as carbon tetrachloride and placed in a small, high-speed Waring Blender or other laboratory mixer, pigments could be dispersed by adding them slowly in the mixer with rapid stirring. Actually, the pigment

TABLE VII

COMPARISON OF CONVENTIONAL MILL COMPOUNDING AND MARING BLENDOR COMPOUNDING
OF DEPOLYMERIZED SILICONE GUM

Pigment	Parts Pigment per 100 of Gum	Mill Compounding			Maring Blendor Compounding		
		Hardness Shore A	Tensile Strength p.s.i.	Elongation %	Hardness Shore A	Tensile Strength p.s.i.	Elongation %
Celite 505	50 (22 volumes)	35	130	135	38	253	197
"	58 25 "	46	220	120	50	431	155
"	75 32 "	55	300	100	66	536	110
"	100 44 "	63	400	95	75	660	85
"	125 57 "	70	470	85	80	750	85
Hi-Sil	53 25 "	62	215	110	63	540	90
"	75 35 "	Cannot be compounded			82	540	50
Celite Super-floss	63 25 "	45	180	125	60	490	125

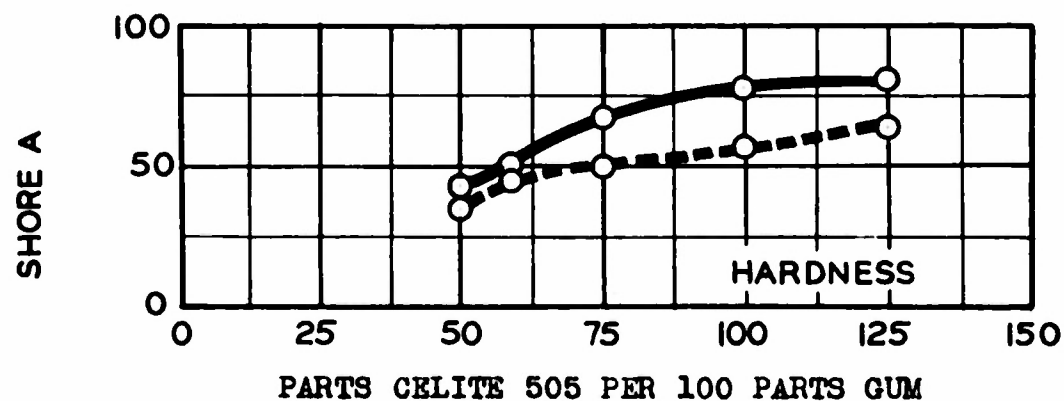
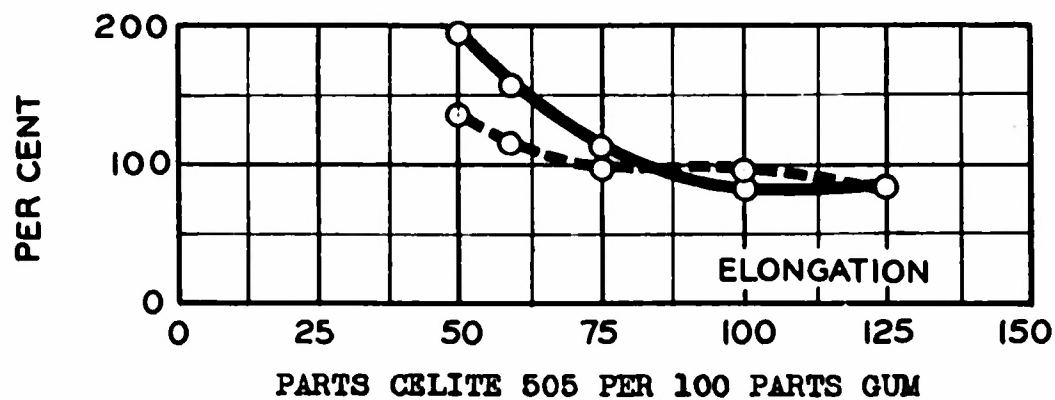
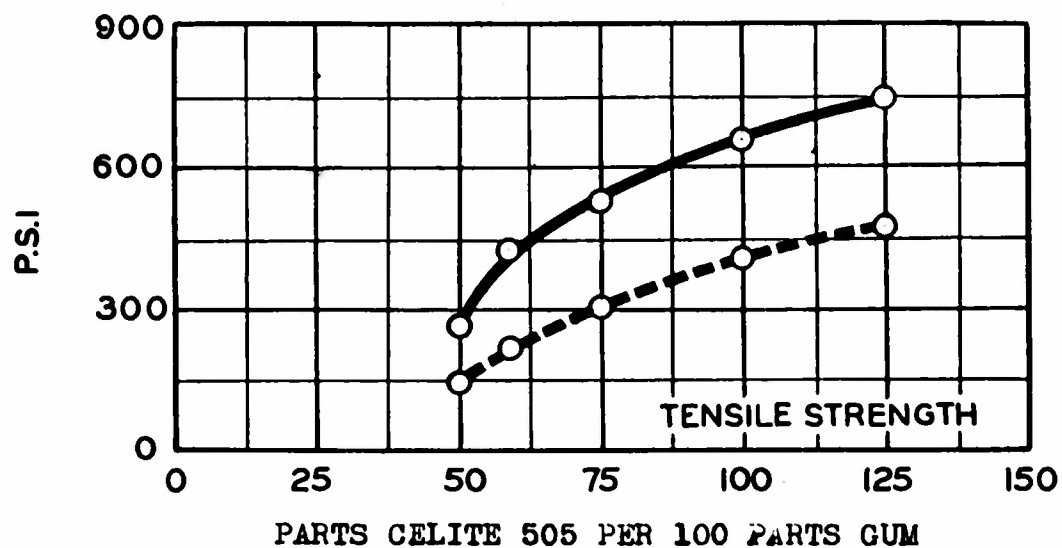
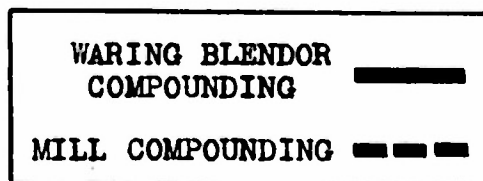


FIG. I - EFFECT OF PIGMENT INCORPORATION TECHNIQUES ON PHYSICAL PROPERTIES



was usually dispersed in carbon tetrachloride, and the liquid rubber was added last. The resulting thin paste was dried to remove the carbon tetrachloride and, incidentally, to repolymerize the rubber. The dried compound was then placed on a mill, dispersion was completed and benzoyl peroxide added. This experiment was carried out several times with Celite 505, Hi-Sil, Celite Superfloss and other pigments. Figure I and Table VII show the improvement in tensile strength and hardness which resulted in the case of Celite 505 when it was compounded in this way in liquefied silicone rubber in the Waring Blender. The increase in tensile strength amounted to as much as seventy-five percent. The only explanation that has been offered for the gain is that improved dispersion and wetting of the pigment occur when the mixture is made in this manner.

Three electron micrographs showing Hi-Sil, zinc oxide and Alon dispersed in liquid silicone rubber are shown in Plate Nos. 3, 4 and 5. Except where the micrographs show the presence of aggregates, it will be noted that the dispersion is good.

Ammonia-Stabilized Liquid Silicone Rubber

It was pointed out above that the liquid silicone rubber would revert to a solid gum if the hydrogen chloride gas were removed by heating or long standing. When the

excess acid was neutralized by the introduction of ammonia gas or ammonium hydroxide, the liquid rubber did not return to its solid form. Instead, it became a relatively stable, liquefied silicone rubber which could be heated moderately without change. The addition of acids to the ammonia-stabilized liquid gum caused a solid rubber to be regenerated. When the ammonia-stabilized liquid was heated for one hour at 300°F., it repolymerized partially to form a sticky solid which had some adhesive qualities. The ammonia-stabilized liquid gum had the same properties as did the acid liquid gum in that it could be compounded with fillers in carbon tetrachloride solution in the Waring Blendor to yield well-reinforced compounds. The ammonia-stabilized product was used as a reactant in the same way as the acid gum in further work.

One sample of the ammonia-stabilized liquid gum was carefully washed to remove all traces of acid, ammonia or ammonium chloride and then was analyzed. The analysis indicated a formula as follows:



A molecular weight determination on this product by a freezing-point-lowering determination in benzene showed a molecular weight of 3206, which corresponds to the above empirical formula. These results indicate that the liquid ammonia-stabilized siloxane consists of either

linear siloxanes of medium length or cyclic siloxanes. The product is undoubtedly a mixture of such polymers. It is very likely that the cyclic polymers predominate, thus accounting for the stability of the ammonia-stabilized liquid product.

Chlorination of Liquid Silicone Rubber

This phase of the work was undertaken to introduce polar groups into the silicone molecule. It was recognized that the lack of polar groups on the silicone chain is responsible to a large degree for its good low-temperature properties, but it was thought that the introduction of a few such polar groups might in some way increase the forces between rubber molecules or between rubber and pigment so as to increase tensile strength.

The liquefied silicone rubber offered a method of reacting chlorine with the rubber, since it could be dissolved in a solvent through which chlorine could be passed. A large number of chlorination experiments were carried out with this liquid 87-79. Chlorine was passed into the solution until the rubber showed the presence of a maximum of one chlorine atom for every four silicon atoms. It was found that the polar chlorine atoms were responsible for an increase in tensile strength from approximately 200 p.s.i. to 600 p.s.i. Meanwhile, the elongation dropped from approximately 125 percent to approxi-

mately 50 percent, and hardness increased from 50 to 90. Not all of the qualities of the chlorinated silicone rubber were favorable, however, because it was found that at the higher oven temperatures (300-400°F.) the chlorinated samples became hard and brittle and there was an odor of chlorine around the oven. This indicates that the chlorinated methyl groups are not stable at these temperatures.

A further study was made of the chlorination of GE 9979-S rubber. Swelling tests were carried out in A.S.T.M. Oil No. 3 to see if the chlorinated samples had improved oil-resistance. It was found that the chlorinated samples swelled slightly more than unchlorinated silicone rubber in A.S.T.M. Oil No. 3. This was not understood at the time, but later work on the mechanism of swelling of silicone rubber, carried out by Mr. R. L. Hauser, demonstrated that swelling is dependent primarily on the cohesive energy density of the swelling liquids and of the rubber itself. Although the substitution of chlorine in the silicone molecule may be expected to raise the cohesive energy density, it is apparent that the cohesive energy density of A.S.T.M. Oil No. 3 is so close to that of the chlorinated rubber that considerable swelling occurs.

Attempts were made to cure the chlorinated rubber

with zinc oxide, magnesium oxide and litharge. Cures were obtained but the tensile strengths were inferior to those obtained with benzoyl peroxide, and this avenue was not pursued further.

It was demonstrated and reported herein that the SE-76 rubber could be easily chlorinated. The chlorinated SE-76 rubber showed improved tensile strength, lower elongation and higher hardness than had been observed with SE-79. This method of modifying silicone rubber in order to improve its strength was abandoned at this time and later resumed under another government contract, NOas 51-766-c. Study under the latter contract has revealed that chlorinated silicone rubber is definitely more resistant to aromatic fuel than the unchlorinated rubber. There is a good probability that chlorinated silicone rubber will have some practical application.

Reaction of Liquid Silicone Rubber with Glycerol, Propylene Oxide, Maleic Anhydride:

The reactions discussed here were actually a continuation of the attempt to prepare a stearic acid analogue mentioned earlier, but the work was also pursued with the thought that some of these modifications might improve the inherent strength or change the behavior of the rubber toward reinforcing agents.

The most interesting was a reaction product of the

liquefied gum with glycerol. The two materials were heated together, at a gradually rising temperature, up to 130°C., at which point all of the acid fumes had been evolved. This mixture would solidify upon cooling to form a repolymerized product containing approximately ten percent glycerol. If the reaction were carried out in the presence of carbon tetrachloride as a solvent and also in the presence of a water layer, the final product was a viscous, colorless, stable liquid. It appears that sufficient glycerol reacts with the depolymerized rubber to replace chlorine end groups with glycerol end groups, and that this permanently stabilizes the liquid rubber. This product was called G-2 and was made later in considerable quantities for use in the production of diaphragms of silicone rubber. It was found that treating the glass fabric of such diaphragms with G-2 before applying the silicone rubber greatly improved the flex life of the final product.

Tests were carried out which revealed that as much as five percent of the G-2 product in the standard silicone test formula had a plasticizing action on the product, lowering tensile strength slightly, raising elongation and lowering hardness. It was thought at this time that G-2 was a permanent liquid, but later tests showed that at a sufficiently high temperature it would harden and

form a rubbery gum on glass fibers.

In the case of propylene oxide, it was expected that this material would pick up free hydrogen chloride to form the chlorhydrin which would evaporate off, thus regenerating the gum. It was found that this did occur, and the resulting gum products were tested. The average product produced in this work had a tensile strength of 400 p.s.i., an elongation of 175 percent and a hardness of 52, indicating that the original properties of the gum had been adequately restored.

Maleic anhydride was heated with depolymerized GE 9979G gum for 30 to 40 minutes at 100°C. Pale yellow gums resulted which, after being washed to remove excess maleic acid, were compounded with 25 volumes of Celite 505 and two percent benzoyl peroxide in the usual way. Results of physical tests were not greatly different from those of the control, indicating that although a small amount of maleic anhydride may have reacted with the depolymerized rubber, it had no appreciable effect on the nature of the rubber.

Further Studies of Depolymerization and Polymer Modification

The above four paragraphs describe reactions of liquid silicone rubber with various substances. It was apparent that none of the products of these reactions contained very much of the reacting substance. Since reaction had

undoubtedly taken place, it was felt that this was due to a lack of sufficient end groups on the liquid silicone rubber. Determination of chlorine in several samples of liquid silicone rubber showed chlorine contents ranging from 0.36 to 0.98 percent. Assuming that there is a chlorine atom on half of the end groups, the calculated molecular weight of the depolymerized silicone rubber runs from 20,000 to 7,000. Molecular weight determinations by the freezing point depression of benzene varied from 2,800 to 1,100. This indicates that the hydrogen chloride transfers from one molecule to another, splitting the chain as it does so, and that some of the chain ends join up to form cyclic, low-molecular-weight polymers. The latter, of course, would be relatively unreactive to agents such as ammonia, glycerol, propylene oxide and maleic anhydride. For this reason, a thorough study of polymer modification was undertaken. The account of this study is copied below from Report No. 9. It was found that depolymerization should be carried out in the presence of a substance such as an anhydride in addition to the acid catalyst in order to prevent ring formation.

Three possible ways in which the silicone skeleton could be altered to produce modified polymers have been studied:

(a) Oxidation of side chains

TABLE VIII

Oxidation of Depolymerized Gum

<u>Run</u>	<u>Silicone Material</u>	<u>Oxidant Used</u>	<u>Reaction Time</u>	<u>Temp.</u>	<u>Results</u>
1.	50g HCl depolym. 9979-G	Aqueous KMnO_4 28.4g	5.75 hrs.	50- 60°C.	Chlorine liberated.
2.	100g HCl depolym. 9979-G	Aq KMnO_4 28.4g	4.25 hrs. at 5.0 hrs.	50-60° 100°	Chlorine liberated. Only part of the oxidant used.
3.	37.1g HCl depolym. 99.79-G	20g CrO_3 in 12 ml H_2O & 32 ml HOAc	10 hrs.	112°	Only the first 5ml of oxidant re- acted, probably due to Cl.
4.	100g Methanol- stabilized oil. (HCl gum reacted with MeOH)	50g $\text{Pb}(\text{OAc})_4$	13 hrs.	120- 140°	All the $\text{Pb}(\text{OAc})_4$ was consumed as shown by a neg. starch-iodide test, but no apparent vis- cosity increase occurred.
5.	100g of Methanol- stabilized oil. (same as in Run #4).	81.3g PbO_2	4 hrs. at 7 hrs. at	140° 190- 210°	No reaction. Not even the first 8.g of oxidant add- ed was consumed (positive starch-iodide test)

- (b) More thorough depolymerization of silicone chains
- (c) Attempts to form a Grignard derivative through the chlorine-substituted side chain

"Items (a) and (c) were not studied extensively, while (b) was. As far as depolymerization is concerned, the groundwork has now been laid for a program wherein short silicone chains of average molecular weight of about 500 can be reacted with other difunctional chain-forming molecules to make mixed polymers with properties quite different from those of the silicones themselves.

Side Chain Oxidation

"One point of attack in an attempt to modify the methyl siloxane polymer is the side chain. While there are numerous reports in the literature that air at high temperatures causes oxidation of siloxanes with replacement of the side chain by oxygen and consequent cross-linking, there is little work reported in the literature on the effect of the usual chemical oxidants. It was noted in earlier work (Report No. 6) that selenium dioxide has a curing action, and hence various other oxidants were tried.

"At first, reactions of depolymerized gum with aqueous oxidants were attempted. It was found that potassium permanganate and chromic anhydride have no effect other

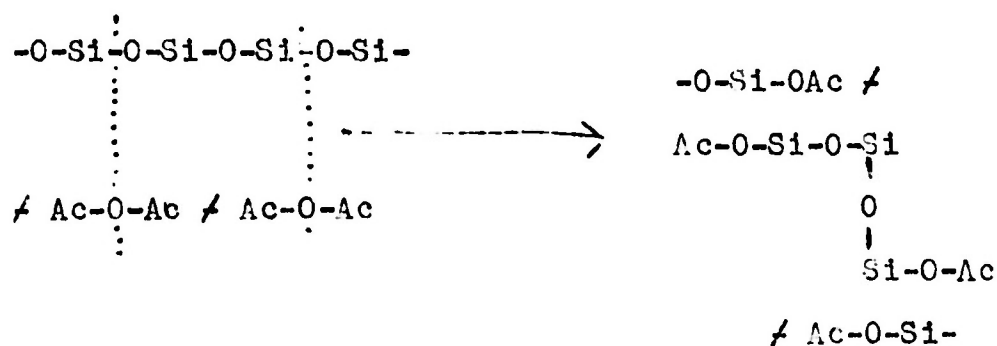
than the oxidation of end group chloride to chlorine. Two points then became apparent: first, if any oxidation were to succeed, it would have to be at a higher temperature than that of the aqueous oxidants used; and second, the gum should first be converted to an intermediate which would be much more stable toward repolymerization than the acid-depolymerized product.

"The methanol-stabilized gum with end methoxyl groups (See page 39) is such a product. Two oxidants which promised to be representative of specific and non-specific oxidants are lead tetra-acetate and lead dioxide. The former reacted with the methoxyl oil, but, in the process, acetic acid was formed. This, together with impurities of acetic acid and acetic anhydride in the commercial lead tetra-acetate, prevented a high-temperature oxidation (because of their volatility) and liberated methanol which consumed the oxidant. The lack of increase in viscosity substantiates this view. With the second oxidant used, lead dioxide, a high reaction temperature was obtainable (190-210°C.). However, in this case, no reaction had taken place at the end of seven hours. The conclusion drawn from this work is that the side chain is extremely resistant to high-temperature, dry oxidation as well as to attack by the common aqueous oxidants.

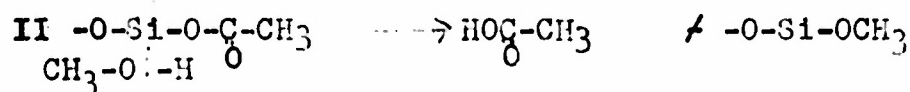
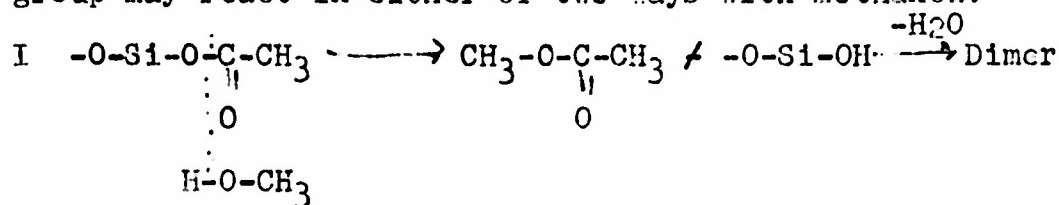
Depolymerization Study

"A second approach to polymer modification was that of extensive depolymerization and incorporation. It may be remembered that it was stated in the Summary of Report No. 7 (see page 32) that the failure to modify the gum by reaction of various substances with the HCl depolymerized gum might be caused by a low number of reactive end groups, or, in other words, by an insufficient degree of depolymerization. The present study was therefore started with two main objectives: first, a more effective means of depolymerization was to be found; and second, these highly depolymerized products were to be evaluated as intermediates for the incorporation of hydroxyl and amino compounds. For the first objective, it was decided to use the freezing point depression method of molecular weight determination as a yardstick.

"The first method of depolymerization was the reaction of acetic anhydride with HCl-liquefied gum in the presence of an acid catalyst, such as ferric chloride ("acid" in the Lewis sense of the word). The over-all reaction may be represented as follows:



It may be noted that this "chain-chopping" results in a depolymerized product with acetate end groups. Since the product is contaminated with excess acetic anhydride from which it cannot be separated by chemical means, a molecular weight determination cannot be run directly on it. However, a reaction of the acetic anhydride oil with methanol produces a methoxylated oil which can easily be freed of impurities (methanol, methyl acetate and acetic acid) by water extraction and hence is ideal for a molecular weight study. The assumption that the methoxyl derivative has the same molecular weight as the acetic anhydride precursor is not valid, since the acetate end group may react in either of two ways with methanol:



However, the maximum increase in molecular weight would be onefold. The molecular weights of the resulting methoxyl-siloxane mixture ranged from 499 to 1070, the lowest values resulting from the highest concentrations of the "chain-chopper", acetic anhydride. Zeisel methoxyl determinations indicated that the oils do, indeed, contain substantial amounts of methoxyl end groups. The determi-

nations, however, were not in agreement with the physical molecular weight values. A typical preparation of a methoxyl oil by way of the acetic anhydride intermediate oil is as follows:

"To 50 grams of gum well-depolymerized by HCl treatment is added 10 grams of acetic anhydride. The mixture is warmed on a hot plate, and 0.2 grams of ferric chloride is added. Although two liquid phases form initially on mixing, after 5 minutes of heating, only one phase remains. The solution darkens and becomes very mobile. Heating at the boiling point is continued for two hours. After cooling, the product is a clear, mobile oil; some dark solid (probably ferric acetate) has settled to the bottom of the flask and may be filtered off.

"Twenty milliliters of this acetic anhydride product is then mixed with 50 milliliters of methanol. The mixture is boiled for 30 minutes. After being cooled, the mixture is repeatedly extracted with water to remove all methanol, methyl acetate, ferric chloride, acetic acid and acetic anhydride. A clear, mobile oil results after drying.

TABLE IX

MOLECULAR WEIGHT DETERMINATIONS ON
METHOXY-OILS FROM ACETIC ANHYDRIDE-OILS

Run	ZAc_2O Used	MW	Run	ZAc_2O Used	MW
1	80	499	3	30	721*
2	40	705	4	10	1070

*The molecular weight as calculated from a methoxyl determination was 270

"The second method of depolymerization was by reaction of the HCl-liquefied gum 9979-G directly with methanol in the presence of an acidic catalyst (here, ferric chloride). All of the reactants were brought together in one phase by means of a solvent such as ether or carbon tetrachloride. The reaction is:



Since water is a product, it was thought at first that a drying agent would increase the extent of reaction. It was found, however, that the amount of drying agent (Drierite was used) had no effect on the molecular weight of the product. A typical preparation of these methoxyl oils is as follows:

180 grams of HCl-depolymerized gum is mixed with 450 milliliters of methanol. 1.5 liters of carbon tetrachloride is added, effecting formation of one phase. Anhydrous sodium sulfate (76 grams) and 1.8 grams of ferric chloride are added to give a yellow solution. After standing at room temperature for five days, the solution is thoroughly washed with water to remove methanol and ferric chloride. The carbon tetrachloride solution of the product is dried over sodium sulfate, and the carbon tetrachloride is distilled off to leave 175 grams of a mobile, colorless oil.

TABLE X

MOLECULAR WEIGHT DETERMINATIONS ON
METHANOL-DEPOLYMERIZATION PRODUCTS

Run	Weight of Drierite (CaSO ₄)	M.W. of the Product
1*	25	336
2*	200	318
3*	400	381****
4*	750	392
5**	0	378
6***	---	1750
7***	---	2035

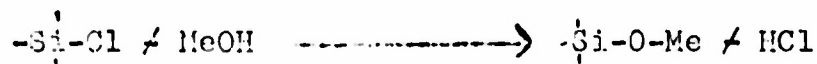
* Runs 1 through 4 were with 50ml MeOH, 0.2g. FeCl₃, 20g. Liq. Gum, all in 100ml dry ether, with the indicated amount of Drierite.

** Run 5 was made with water-saturated ether.

*** Runs 6 and 7 (controls) involved the direct reaction of HCl-liq. gum with excess MeOH without solvent, acid catalyst, drying agent, etc.

****The molecular weight as calculated from a Methoxyl determination was 1020.

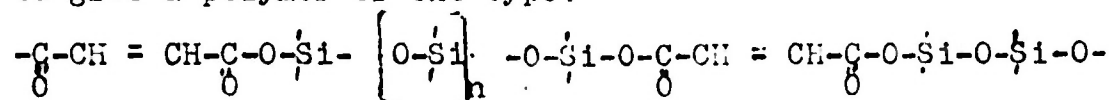
The reaction involved in runs six and seven is:



The low content of methoxyl in Run No. 3 indicates that cyclization may have occurred following depolymerization. This would account for the presence of small molecules containing no methoxyl end groups. The conversion of the HCl-depolymerized product into low-molecular-weight methoxy derivatives makes possible a comparison of the products of the two new depolymerization methods with the HCl liquid gum. It is significant that values around

1800 have been obtained in the past for the HCl-depolymerized liquid gum without stabilization.

"These two depolymerization methods appear to be general; that is, any anhydride should react with the gum in the presence of an acid catalyst. The anhydride of a dibasic acid (as maleic anhydride) should react in the presence of an acid catalyst and in a homogeneous system to give a polymer of the type:



That this was not effected in earlier work (Report No. 6) is probably due to the failure to use an acid catalyst and to obtain a one-phase system.

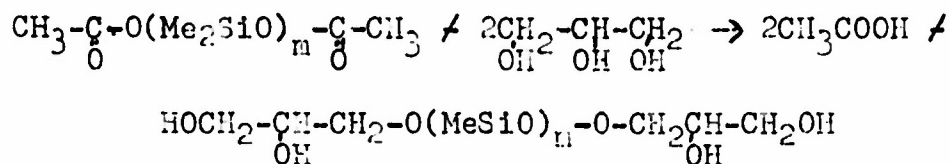
Silicone Modification

"After the two new methods of depolymerization had been explored, the problems of incorporation of foreign groups into the siloxane molecule and repolymerization were studied. Unlike the methoxyl oils which seem relatively unreactive, possibly because of a paucity of end groups, the acetic anhydride products reacted readily with hydroxyl compounds such as methanol and glycerol. This is in accordance with theory, which states that the methoxyl compounds are analogous to esters, and the acetic anhydride products to mixed anhydrides.

"The reaction with glycerol is analogous to the

reaction with methanol, which has already been discussed.

It may be represented as follows:



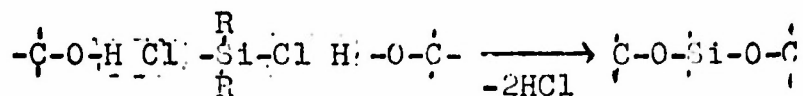
It is to be anticipated that some linear chain formation and some cross-linking also occur through the β -hydroxyl groups of the glycerol. The products formed by this reaction of glycerol with the acetic anhydride oils are colorless, mobile liquids. They cannot be transformed to gums by ordinary methods; that is, neither 2 percent ferric chloride nor traces of sulfuric acid will cause appreciable polymerization as occurred with the earlier reactions of this kind (Report No. 7). This is probably due to a preferential reaction of free hydroxyl groups with the acidic catalyst. Treatment of the oil with excessive amounts of concentrated sulfuric acid followed by dilution with water does result in gum formation, this probably being effected by the elimination of glycerol groups. A typical glycerol-oil preparation is as follows:

400 grams of HCl-depolymerized gum is placed in a liter Erlenmeyer flask. To this is added 1. gram of ferric chloride (hydrate) and then 20. milliliters of acetic anhydride. The contents of the flask are heated on a hot plate with stirring for a few minutes.

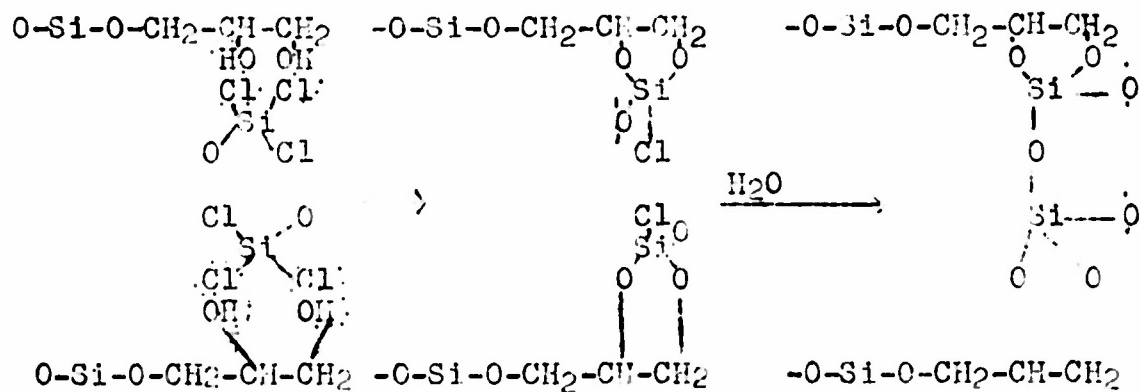
Within five minutes, 20. milliliters of acetic anhydride is added. Then 160. milliliters more acetic anhydride is added evenly over a period of one hour, and the mixture is boiled for one additional hour. After the flask and contents have cooled, the solution is filtered to give a clear, red mobile liquid (the acetic anhydride product). To this is added 200. milliliters of glycerol, which forms a yellow lower layer. The mixture is heated cautiously with stirring to initiate the reaction, which proceeds exothermically. In ten minutes, a dark lower phase forms with a clear oil above it. The mixture is heated on a hot plate for one hour and is then allowed to cool. The dark, water-soluble lower phase is discarded. This probably consists of glycerol mono- and di-acetates, unreacted glycerol and highly hydroxylated organo-silicone products. The top phase is clear; this is repeatedly water-extracted after dilution with ether. The ether solution is dried over sodium sulfate and the ether is distilled off to give a clear, colorless mobile oil (Glycerol Product), 390 grams yield.

"The glycerol products can be condensed by reaction with cross-linking agents as diisocyanates and polyfunctional chlorosilanes. The condensation process is

probably not as simple as:



since, when tried, dimethyldichlorosilane did not effect gum formation. Gum formation occurred on reaction with phenyltrichlorosilane and may follow the path:

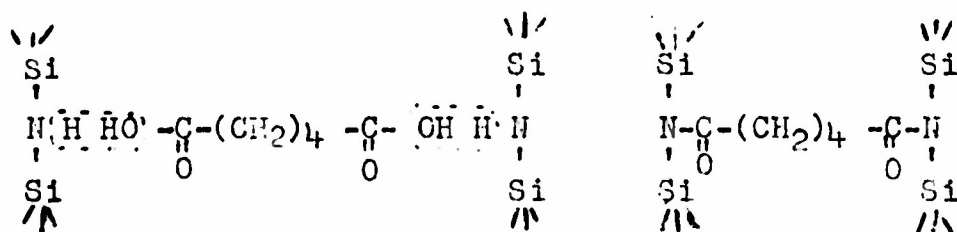


This mechanism rationalizes the failure to cross-link with dichlorosilane, for a dichlorosilane would act as a chain stopping agent. These gums, unlike the untreated glycerol products, may be cured; however, the products are brittle and weak. By varying the amount of phenyltrichlorosilane, one obtains gums of varying hardness. With 2.5 percent, an oil was obtained. With 10 percent, a greasy mass was produced. With 13 to 25 percent, hard gums were obtained. In a typical run, 40. grams of glycerol product, prepared by the above procedure, was reacted with 7.5 grams of phenyltrichlorosilane by heating the homogeneous mixture under reflux for four hours.

During this period, hydrogen chloride was evolved. At the end of this time, the liquid was cooled and stirred with excess water, forming a solid, rubbery but brittle gum.

"In the case of the methoxyl oils, repolymerization is effected by heating with 2 percent ferric chloride. One batch of gum so formed showed exceptional hardness on curing; however, repetition of the procedure gave a dry brittle product. Two points are evident: first, although chemical procedures may be repeated to give the same product, the gumming process has not been standardized and is subject to variations in human judgment; and second, the anomalous hardness of the methoxyl gum was probably due to a difference in the degree of repolymerization and not to a change in the basic polymer type.

"Another approach to polymer modification was the reaction of ammonia-stabilized liquid gum with adipic acid to form cross-links. The reaction is probably as follows:



This represents an unstable structure analogous to a beta diketone. The product, while it appeared to be a strong gum after the reaction, proceeded to depolymerize slowly

to give a product similar in appearance to the original ammonia-stabilized liquid. The addition of triethanolamine failed to prevent this decomposition. The method of preparation of the adipic acid ammonia-stabilized silicone product is as follows:

Eleven grams of adipic acid is mixed with 122. grams of ammonia-stabilized gum (solvent having been removed). The mixture is heated to 250°C. on a hot plate for five hours. Some of the adipic acid sublimes and condenses on the flask walls and must be scraped off. At the end of the reaction period, the liquid is allowed to cool, and a strong elastic gum forms. On standing for a week, this gum decomposed to form an oil. Addition of nine grams of triethanolamine did not prevent depolymerization.

Formation of Grignards

"In an attempt to modify the polymer by introduction of polar groups, chlorinated 81176 gum (1 Cl to 4 Si atoms) was treated with excess magnesium. There was no indication of Grignard formation except in one case where the polymer separated from ether solution, indicating cross-linking. This work might be repeated with conversion to the iodo-derivative before attempting to form the Grignard reagent. It should be noted, however, that there are reports in the literature on the depolymerization of

methyl silicones by Grignard reagents."

Following the study of depolymerization reported in the last few pages, further work might have been done on reactions of the thoroughly depolymerized rubber with ammonia, glycerol and other reactive substances in an effort to improve the reinforcement of the silicone polymer. However, other interesting and fruitful experiments were already under way, which made it necessary to curtail this work.

Reclaiming

After it had been demonstrated that strongly acidic substances such as titanium tetrachloride would liquefy large quantities of silicone rubber, it was obvious that this should be tried on vulcanized silicone rubber, as a method of reclaiming. The first experiment was carried out with silicone-coated glass cloth. Silicone-glass cloth gasket scrap was digested first in a ten percent solution of titanium tetrachloride in carbon tetrachloride. The concentration of titanium tetrachloride could be reduced to five percent, but not as low as one percent. Upon standing at room temperature, these solutions attacked the silicone rubber, loosening it from the glass. After the disintegration of the silicone rubber, the glass fiber was removed from the mixture. Then the solution was carefully treated with water to decompose the titanium

tetrachloride, transforming the latter into titanium dioxide. The slurry was concentrated to dryness by evaporation, and the rubbery mass was then milled to disperse the newly formed titanium dioxide.

Reclaim produced in this way was compounded in 50:50 mixtures with new Dow Corning 6-160 rubber. Tensile strength and elongation were definitely reduced with this much dilution by reclaim, although introduction of additional benzoyl peroxide restored the tensile strength to its original value. It was evident that reclaim of some value could be made by this process. A comparison of other reclaiming agents was made and it was found that titanium tetrachloride was the best, followed in order by dimethyldichlorosilane, stannic chloride and silicon tetrachloride.

In order to evaluate the reclaiming process further, these tests were repeated. In this case, the scrap for reclaiming was selected free of glass fiber, and one half of the scrap was reclaimed with titanium tetrachloride while the other half was reclaimed simply by grinding extensively on the laboratory mill. A very fine powdered scrap was produced in this way.

The two reclaims were then compared by putting each in 50:50 mixes with Dow Corning 6-160. It was found that the ground scrap produced very little lowering of the tensile strength and elongation, as compared with

those of the control compound. The solution reclaim, on the other hand, showed a large reduction in elongation and a large increase in hardness. Tensile strength was not greatly affected. The conclusion was drawn, therefore, that reclaim produced by the solution process offers no advantage over reclaim produced simply by grinding. Grinding may not be feasible on scrap containing glass fiber because of the difficulty of grinding such a material and because the ground glass in the product will have little value. It would seem, however, that in order for the solution process to be very practical, the silicone content of the scrap should be high. The usual varieties of silicone-coated glass cloth contain generally less than 10 percent of gum. Reclaiming this by the solution process, as now developed, is questionable economy.

Adhesives

Another by-product of the work on depolymerization was the possibility of making a silicone adhesive from the ammonia-stabilized liquid rubber. When this material was heated for one hour at 300°F., a sticky product was obtained which, however, had very little cohesive strength. Upon getting further into this problem, it was found that greater strength in the adhesive could be obtained by blending new SE-76 rubber with silicone oil, and the strength could be enhanced further by adding small amounts

of filler and benzoyl peroxide. The best formulation, called Adhesive #200, consisted of four parts of SE-76 rubber, six parts of G.E. 9996-1000 silicone oil, 0.17 parts of Santocel C, 1.53 parts of Titanox RANC and 0.2 parts of benzoyl peroxide. This mixture was coated on glass tape which was then heated in an oven in air for one half-hour at 350°F. This product stuck to a wide variety of substances, including glass, metal, wood, silicone rubber and GR-S rubber. It remained sticky over a temperature range from -70° to 480°F. After being applied, the tape could be exposed to boiling water, air at -70°F., air at 480°F., and ASTM Oil No. 1 at 350°F., without losing adhesive properties. This work was partially responsible for our entering into a contract with the Air Force on the development of low-temperature adhesives (AF33(600)-16213).

Isocyanates as Cross-Linking Agents in Silicone Rubber

Isocyanates are very active chemicals in which the -NCO groups can react readily with compounds containing -OH or -NH₂ groups. Di- or poly-isocyanates have been used to produce polymers because of this reactivity; for example, a diisocyanate will react with ethylene glycol to form a long-chain polymer. If glycerol is used in place of ethylene glycol, the polymer will be three-dimensional. Resins may be formed by reacting organic diisocyanates

with siloxanes which contain active hydroxyl groups (U.S. Patent 2,527,590, 1950). In Report No. 9, the results of a study of the reaction of meta toluene diisocyanate with ammonia-stabilized and with glycerol-stabilized liquid silicone gum were presented. It was found necessary to be sure that the reactants were free of moisture, since water decomposes the diisocyanate. About twenty different rubbery products were produced by allowing the gum to react with 5 to 25 percent of the diisocyanate.

The product resulting from the ammonia-stabilized liquid gum was given special study. It was found that it could be milled in the usual manner and compounded with as much as 50 volumes of Celite 505. When cured in a press for 15 minutes at 250°F., the compounds resulted in crumbly slabs when cured either with or without benzoyl peroxide.

The glycerol-stabilized liquid gums were also given special study and they, too, were found to be capable of being milled and loaded with Celite 505 (25 volumes). These compounded gums became brittle and nonelastic when heated in the press, as above, either in the presence or absence of benzoyl peroxide.

It was concluded that the diisocyanate reacts with the active $-NH_2$ or $-OH$ groups of ammonia-stabilized or glycerol-stabilized liquid gum, but no obviously useful products resulted.

Reinforcement of SE-76 Silicone Rubber

It was pointed out earlier that liquefying SE-79 rubber, followed by dispersion of fillers in it in carbon tetrachloride solution, resulted in improved reinforcement. When the General Electric Company made available a liquid silicone rubber, SE-76 (originally 81176), it was thought likely that improved dispersion of fillers would be possible with it.

SE-76 gum is a water-white, viscous liquid which smooths out on the mixing rolls immediately. Unlike SE-79, it is not cross-linked to any great extent. For this reason, it is soluble in hydrocarbons, chlorinated solvents and methylethylketone. At the time that this work was started, the exact composition of SE-76 was not known to us. An infrared examination of the material at a later date proved that it is substantially 100 percent pure polymer of dimethylsiloxane. We also learned later that it is polymerized in the presence of alkali hydroxide. During the past two years, it has been supplied in various viscosities. The earlier samples were quite heavy, and General Electric found that when compounded, the mixtures were too stiff for convenient processing. Early in 1952, therefore, they lowered the viscosity of the product to its present level. Molecular-weight figures which characterize the degree of polymerization will be reported later in this report. It may be said here that the early product

TABLE XI (cont.)

Pigment Cmpd. #	Vol. Pig.	Cum. Mins.	Press Cure	Of. Hrs.	Oven Cure	Stress (200%)	T	E	K	Report & Page	% B.P.
Whitetex 2260-2	20	SE-76	150230		10300		263	250	28	12-16	2.0
2260-3	30	"	"	"	"		410	212	42	"	"
2267-2	60	"	"	"	"		390	112	72	"	"
Whitcarb 1849	40	SE-79	150250		"		260	503	36	8-20	"

R

TABLE XI (cont.)

Pigment Cpd.#	Vol. Pig.	Gun	Press Cure Hrs.	Gun	Press Cure Hrs.	Stress C	T	E	H	Report & Page	% B.P.	
Si-O-Lite	20	SE-76	150	250	10	300	368	434	263	46	10-5	2.0
Santocel C	5	"	150	230	"	101	168	300	27	10-7	"	"
	10	"	"	"	"	212	536	333	40	"	"	"
	15	"	"	"	"	390	362	342	50	"	"	"
	20	"	"	"	"	481	337	308	61	"	"	"
	25	"	"	"	"	533	576	225	71	"	"	"
	27.5	"	"	"	"	582	654	263	73	"	"	"
Spheron 6 Black	20	"	150	250	160	400	107	175	30	10-28	4.0(T.B.P.)	"
	25	"	"	"	"	"	258	200	39	"	"	"
	40	"	"	"	"	"	424	175	68	10-29	"	"
Titanox RAC	20	SE-79	"	"	10	300	245	325	38	8-23	2.0	"
	40	"	"	"	"	"	537	408	46	"	"	"
	60	"	"	"	"	"	462	288	56	"	"	"
Titanox RC	40	"	"	"	"	"	249	400	43	"	"	"

TABLE XI (cont.)

Pigment Cpd.	Vol. Ptg.	Guar	Press Cure Mins.	Of. Hrs.,	Oven Cure °F.	Stress C 200%	T	E	H	Report & page	% B.P.
H1-S11 2244	10	SE-76	150230		16300	137	344	417	31	12-14	2.0
52-MHB-42	15	"	"	"	"	308	712	363	37	"	"
	20	"	"	"	"	482	757	300	42	"	"
H1-S11 2278	10	"	"	"	"	128	436	613	30	"	"
C.V2	15	"	"	"	"	200	500	580	46	"	"
	20	"	"	"	"	217	432	400	60	"	"
	25	"	"	"	"	373	374	250	72	"	"
H1-S11 2245-1	15	"	"	"	"	189	392	500	40	"	"
G	20	"	"	"	"	152	361	587	53	"	"
	20	"	150250	"	"		579	242	50	8-30	"
H1-S11 1761-1	20	"	150230	"	"		206	187	40	12-9	"
Hicalith ^G 2183-3	30	"	"	"	"						
Rayox 1825	20.2	SE-79	150250	"	"		252	325	40	8-23	"
110	1826	"	"	"	"		542	475	43	"	"
	1844	"	"	"	"		548	333	52	"	"
Super Multi-Flex	1628	"	"	"	"		218	638	35	8-20	"

TABLE XI (cont.)

Pigment Cpd.#	Vol. Fig.	Gum	Press Cure Mins., OF.	Oven Cure Mins., OF.	Stress C 200%	T	E	H	Report & page	% B.P.
Alon 1961-3 II	30	SE-76	15@230	1@300	108	216	375	30	9-5	3.0
Aerosil 1901	15	"	15@250	"	"	607	167	70	8-31	2.0
1901-1	"	"	"	"	"	673	175	70	"	3.0
1901-2	"	"	"	"	"	633	150	70	"	4.0
Burgess 2104-3 Iceberg	30	"	15@230	"	"	382	200	35	12-8	2.0
Celite 2103-2 318	40	"	"	"	75	213	1050	16	12-5	"
Celite 2325-2 270, fine	40	"	"	"	"	532	100	62	13-4a	2.0
Celite 2101 800	10	"	"	"	77	229	438	19	10-5	"
Celite 1770 Super Floss	40	"	15@250	"	"	472	200	64	8-4	"
Davison --- Silica	10	"	"	"	106	253	338	24	9-5	"
GS199S 1967-4	25	"	"	"	335	1285	625	70	10-43	"

TABLE XI

SUMMARY OF REINFORCEMENT EXPERIMENTS, SP-76 RUBBER

Pigment Cpd.#	Vol. Fig.	Gum	Press Cure Min., of.	Oven Cure Hrs., of.	Stress C 200%	T	L	H	Report & page	% B.P.
Alon	0.0	SE-76	15@230	1@300	--	29	150	10	9-19	2.0
	5	"	"	"	66	209	563	20	"	1.8
	10	"	"	"	162	702	733	33	"	3.0
	15	"	"	"	155	558	850	39	"	3.5
	20	"	"	"	381	521	413	60	"	4.0
Hydrated 1908-2 Al C-741	40	SE-79	15@250	1@300		217	917	32	8-32	2.0
Hydrated 1907-2 Al C-740	40	"	"	"		221	858	30	"	"
Hydrated 1906-2 Al C-73C	40	"	"	"		232	808	30	"	"
AZO-ZZZ-66 1837	20	"	"	"		330	475	42	8-22	"
1834	60	"	"	"		198	1100	53	"	"
AZO-ZZZ-55 1822	18.8	"	"	"		365	513	43	"	"
1823	37.6	"	"	"		436	507	52	"	"
1840	60	"	"	"		398	350	65	"	"

had a molecular weight of approximately 700,000, and the present product has a molecular weight in the 400,000 range.

Whereas it was extremely difficult to reach a tensile strength of 500 p.s.i. with the SE-79 polymer, this figure was reached with the new rubber with several pigments. One tensile figure reported in Report No. 8 was 1034 p.s.i. Results such as these were obviously encouraging.

Table XI facing this page, is a summary of all of the experiments which were carried out with fillers in SE-76 rubber. In most cases, the fillers have been described previously in Table I. Properties of those not mentioned in Table I are described in Table XII. The data selected for Table XI include for most pigments the results which were obtained at a volume loading which gave optimum tensile strength or elongation. For those fillers which appeared to have outstanding properties for one reason or another, additional data at other volume loadings are also supplied in this Table.

Pigments tested at once in SE-76 included Alon, three forms of titanium dioxide, two zinc oxides, two calcium carbonates, a new silica pigment known as Aerosil, and others. It may be said here that these pigments fall generally into two classes: those producing moderately high tensile strength and very high elongation, and those producing moderately high tensile strength and low

TABLE VII (cont.)

	Supplier	Particle Size	pH	Remarks
Rayox 110 Super Multiflex	R. T. Vanderbilt Diaron Alkali	0.035	7-8 9-10	Rutile CaCO ₃ Stearic Acid Coated 2% Ignition Loss; 3% Sulfate
Si-0-Lite	Mallinckrodt Chemical Works	0.2		
Santocel C	Monsanto Chemical Co.	3-5 0.005-0.015	3.5-4.0	90% SiO ₂ ; 3% Na ₂ SO ₄ ; 1% Al ₂ O ₃ & Fe ₂ O ₃ ; 4-6% volatile Medium Processing Channel
Spheron 6 Black	G. L. Cabot Inc.	.03	4.5	
Titanox RANC	Titanium Pigment Corp.	0.35	6.5-7.5	94% Rutile / Al ₂ O ₃ , ZnO and SiO ₂
Titanox RC Whitetex Witcarb 7	Titanium Pigment Corp. Witco Chem Co.	0.65 0.05	8 11.3	30% TiO ₂ ; 70% CaSO ₄ Fine grade of clay CaCO ₃

TABLE XII

FILLER PROPERTIES

	Supplier	Particle Size	pH	Remarks
Alon	G.L. Cabot Inc.	0.2-0.4		
Hydrated Alumina C741	Aluminum Company of America	0.02-0.04	5.4	Gamma crystalline form
" " C740	" "	0.6		Coated with Stearic Acid
" " C730	" "	0.6		" " Coconut Oil
Zinc Oxide AZO-ZZZ-66	American Zinc Sales Co.	0.6		Uncoated
" AZO-ZZZ-55	American Zinc Sales Co.	0.22	7-8	French Process-Lead free
Alon II	G.L. Cabot Inc.	.005-.1.0	7-8	Am. Process " "
Aerosil	G.L. Cabot Inc.	.015-.020	4.5-6.0	Alpha crystalline form
Burgess Iceberg	Burgess Pigment Co.		5.8-6.3	Degussa Silica Aerogel
Celite 318	Johns Manville Co.			Calcined aluminum silicate
				Super Floss with metallic
				stearate coating
Celite 270; fine (505)	Johns Manville Co.	1-6	7.5	Calcined diatomaceous
				earth
Celite 800	Johns Manville Co.	0.02	9-10	Autoclaved with lime
				slurry
Celite Super Floss	Johns Manville Co.	2-4	10	Flux calcined with Na_2CO_3
Davison Silica	Davison Chemical Co.	6-14		
DuPont CS199S	Grasselli Division DuPont	0.5-2	7.5-9.5	Hydrophobic coated pre-
		0.006-0.014		cipitated silica
H1-Sil 52-MHB-42	Columbia-Southern Chemical Corp.			
H1-Sil CMV2	Columbia Southern Chemical Corp.			Sp. fine ground H1 Sil
H1-Sil C	Columbia Southern Chemical Corp.			
H1-Sil	Columbia Southern Chemical Corp.	0.025	8-9	Hydrated silica
Micalith G	General Mining Assoc.	1-50	6.5	47% SiO_2 ; 36% Al_2O_3

elongation.

Those fillers which are characterized by high elongation in silicone rubber include the following: Alon, hydrated alumina, zinc oxide, Celite 318, Celite 800, GS199S Silica, Hi-Sil C, Hi-Sil CXV2, Super Multiflex and Witcarb R.

Those fillers which are characterized by low elongation include Aerosil, Celite 220, Celite Super Floss, Hi-Sil 52-MAT-42, Hi-Sil, Micalith C, Si-O-Lite, Santocel C, carbon black and Whitetex.

Some fillers seem to fall in neither class, notably the titanium dioxides, of which Rayox 110 and Titanox RANC are examples.

It is apparent that relatively coarse fillers, such as Celite 270, do not show a much greater degree of reinforcement of SE-76 liquid silicone rubber than that obtained with SE-79, as seen in Tables II and III. However, very finely divided fillers, such as Alon, GS199S Silica, Santocel C and Aerosil, are benefited by the use of the more liquid rubber and may result in tensile strengths at least 100 percent higher than those obtained with the earlier rubber.

As will be seen later, with Alon and GS199S Silica suitable proportions of filler make it possible to exceed a tensile strength of 1000 p.s.i. Such effects are not entirely the result of good reinforcement, since both Alon

TABLE XIII

PROPERTIES OF PIGMENTS

	<u>Titanox RANC</u>	<u>Santocel C</u>	<u>GS199S</u>	<u>Alon</u>
TiO ₂	94%			
SiO ₂	Present	89.5 - 91.5%	84 - 88%	
Volatile or Organic		4.0 - 6.0%	10 - 16%	
Na ₂ SO ₄		2.5 - 3.5%		
Al ₂ O ₃	Present			99.4%
ZnO	Present			
Fe ₂ O ₃				Present
pH	6.5 - 7.5	3.5 - 4.0	7.5 - 9.5	5.4
Aggregate Size	---	3 - 5.4	0.5 - 2.4	0.2 - 0.4-4
Ultimate Particle Size	0.35 μ	0.005 - 0.015 μ	0.006 - 0.014-4	0.2 - 0.04-4
Surface Area sq. l/g	---	500	300	50 - 70
Bulk Density - Lbs./cu. ft.	260	6	7	4 - 5
Specific Gravity	4.2	2.2	1.98	3.6
Crystalline State	Rutile	Amorphous	Amorphous	Largely gamma crystalline form.

and GS199S Silica affect the cure. Alon tends to deactivate part of the benzoyl peroxide, thus giving rise to high elongation and therefore high tensile strength stocks. GS199S Silica possesses the property of vulcanizing the silicone rubber in the absence of added benzoyl peroxide. When controlled by low temperatures of curing, GS199S Silica, by a combination of reinforcement and vulcanizing activity, can produce stocks with tensile strengths in excess of 1500 p.s.i. and elongations of 500 percent or greater.

Santocel C.

For various reasons, the filler which has come to be considered as standard in SE-76 compound is Santocel C. It is a silica aerogel which is comprised of very small (.01 micron) ultimate particles which are formed in aggregates of 3 to 5 microns diameter. These aggregates are porous and when placed in the rubber they apparently soak up the liquid silicone rubber so that remilling is strongly recommended to overcome the so-called "structure" effect. After being remilled, the compound remains rubbery indefinitely. Either because of its porosity or the presence of water-soluble impurities, Santocel C imparts very poor water-resistance. For all other applications, Santocel C compounds are excellent. Properties of Santocel C are given in Table XIII.

This pigment at a 20-volume loading results in a tensile strength of 900 p.s.i., and elongation of 300 percent and a hardness of 61 (Table XI). It falls in the class of low-elongation pigments for silicone rubber. Inasmuch as Santocel C provides moderately high tensile strengths and elongations, it has been adopted for use in some of the General Electric silicone compounds and has been recommended by this company to those who wish to compound their own silicone rubber.

Fillers which are of interest because at high loadings they provide moderate tensile strength and elongation without undue hardening are zinc oxide (AZO-ZZZ-55), titanium dioxide (Rayox 110 and Titanox RANC), Hi-Sil, Celite Super Floss and Celite 270, Whitetex, Witcarb R and Super Multiflex. Since emphasis was placed on striving to achieve high properties, none of these was investigated extensively. Much further study could be placed on some of these, as well as others such as Si-O-Lite and special samples of Hi-Sil, and Micalith G. Aerosil will undoubtedly receive considerable attention since it is to be imported or manufactured by at least two companies in this country. Aerosil is an aerogel silica like Santocel C and will probably be competitive with it in the silicone field. It became available only at the close of the contract, and not much could be done with it for lack of time.

As pointed out above, Santocel C was considered a

standard or control pigment for much of the remaining work. Comments on GS1993 Silica are reserved for later sections of the report.

Alon

The first of the fillers which gave outstanding results was Alon. Details of the characteristics of Alon may be found in Table XIV. A complicating factor is the fact that Alon tends to destroy or inactivate a substantial portion of the benzoyl peroxide. Thus it is generally necessary to add about twice as much benzoyl peroxide when Alon is used as when other reinforcing pigments are used. If this is not done, very soft vulcanizates will result and, in some cases, the slabs will not cure at all. If they do cure at all, long oven cures or high-temperature oven cures may cause reversion. All of these difficulties can be corrected by adding additional benzoyl peroxide. With low percentages of benzoyl peroxide, very stretchy, rubbery products are formed with elongations as high as 1200-1400 percent and tensile strengths from 800-1000 p.s.i. As with most silicones, long, high-temperature oven cures reduce tensile strength and elongation, but in the presence of from three to five percent of benzoyl peroxide, tensile strengths of over 900 p.s.i. with elongations of approximately 600 percent can be obtained. Examples of results obtained with Alon, showing the effects

TABLE XIV

ALON IN SE-76

(Oven Cure 1 hr. @ 300°F.)

<u>Vols. Alon</u> <u>per 100 SE-76</u>	<u>BP</u> <u>%</u>	<u>Tensile</u> <u>p.s.i.</u>	<u>Elongation</u> <u>%</u>	<u>Hardness</u> <u>Shore A</u>	<u>Stress</u> <u>@ 400% E</u>
5	1.4	199	365	34	
5	1.6	204	375	35	
5	1.8	152	250	36	
5	2.0	171	275	34	
10	1.4	362	1050	29	
10	1.6	462	825	32	
10	1.8	465	892	32	
10	2.0	434	742	39	
10	3.0	362	400	41	
15	2.0	868	1407	30	
15	3.0	984	1229	32	

(Oven Cure 8 hrs. @ 300°F.)

15	2.0	736	1065	27	268
15	3.0	962	588	37	535
15	4.0	838	387	42	892
15	5.0	592	350	48	---
20	2.5	142	975	25	66
20	3.0	488	1115	32	166
20	4.0	867	585	42	510
20	5.0	811	400	52	810

of increasing Alon concentrations at constant amounts of benzoyl peroxide, and the effect of increasing cure and benzoyl peroxide at constant loading of Alon are shown in Table XIV, facing this page.

The unusual result when a 10-volume loading gives a higher elongation and lower hardness than a 5-volume loading at 1.6 percent of benzoyl peroxide is an indication of the side reaction of Alon with peroxide. It is corrected by adding additional peroxide. Underlined percentages of benzoyl peroxide are those recommended as sufficient to produce stable cures. In cases where less was used, continued curing caused reversion.

For a time after these results were obtained in 1951, the Cabot Company temporarily abandoned the manufacture of Alon. More recently, they have again become interested in it, and there is a fair chance that it will eventually become commercially available. Alon is treated with hydrochloric acid in one of the final stages of its manufacture, followed by high-temperature calcining to drive off the excess acid, moisture or aluminum chloride. The final pH is about 5.4. As will appear later, further calcining drives off more acidic materials, and the filler becomes less strongly reinforcing (loses modulus) but imparts higher elongations and higher tensile strengths. The affinity of Alon for the silicone rubber is evident in the high elongations obtained.

As an example of what can be accomplished with Alon

TABLE XV

AMG TESTS ON ALON RECIPES

	Recipe <u>1867-5</u>	Recipe <u>2452</u>	3303C <u>Spec.</u>
Unaged			
Tensile, p.s.i.	769	720	400/min.
Elongation, %	367	250	100/min.
Hardness, Shore A	64	58	60±5
Tear-Resistance	118.5	77	35/min.
Aged in A.S.T.M. Oil No. 1 70 hours @ 350°F.			
Tensile, p.s.i.	448 (-42%)	-	-20% max.
Elongation, %	292 (-20%)	-	-20% max.
Hardness	55 (-9)	-	-10 max.
Vol. Change, %	43	-	10% max.
Aged in Air 24 hours @ 450°F.			
Tensile, p.s.i.	580 (-25%)	610 (-15%)	-10% max.
Elongation, %	167 (-54%)	125 (-50%)	-25% max.
Hardness	72 (48)	82 (24)	10 max.
Compression Set 22 hours @ 350°F.			
% of original deflection	93	99	less than 60
Low-Temp. Brittleness			
	passes	passes	lower than -70°F.
	Recipe <u>1867-5</u>	Recipe <u>2452</u>	
SE-76	100	100	
Alon	(20 vol.) 73.6	(15 vol.) 49.2	
Benzoyl Peroxide	5.	4.0	
Press Cure	15 min. @ 250°F.	15 min. @ 230°F.	
Oven Cure	Cycle cure to 480°F.	24 hrs. @ 480°F.	

in practical silicone recipes, the table on the opposite page shows results obtained on two recipes compared with the AMS 3303C specification. These recipes do not meet the specification in all particulars, but certain points are worthy of comment. In the first place, the unaged tensile, elongation and tear-resistance specifications are far exceeded by the two Alon recipes. Losses on aging in A.S.T.M. Oil No. 1 or in air exceed the allowed percentages. However, the properties of the aged rubber are still higher after aging than the specification requires before aging. These two recipes contain no metal oxides which are usually added to impart low compression set, and therefore they do not meet the compression set requirements. No effort was made to revise these recipes so that they would meet the specifications in all respects, since Alon was not available commercially.

Effect of Acid in SE-76 Recipes

An interesting experiment was carried out with the addition of benzoic acid or stearic acid to a recipe containing 100 parts of SE-76, 40 parts of Santocel C and 1.65 percent of benzoyl peroxide. The benzoic and stearic acids were added in amounts of one and two percent, and the samples were all given a thorough oven cure of 16 hours at 400°F. The results clearly showed that these organic acids have a permanent softening or depolymerizing

action during the curing. They reduce tensile strength, raise elongation and lower the hardness. Benzoic acid was less harmful than stearic acid, probably because it is volatilized during the cure. Two percent of stearic acid reduced tensile strength from 800 to 200 p.s.i., and hardness from 40 to 30.

This experiment is important because it shows clearly that the benzoic acid, which is a by-product of benzoyl peroxide vulcanization, has a harmful effect. Apparently, one should avoid adding any acidic material to silicone compounds. One of the hydrated aluminum oxides supplied by the Aluminum Company of America contained particles of pigment which were coated with stearic acid. The harmful effect of the acid was noted here also.

Rate of Vulcanization and Post Curing

An investigation of the rate of vulcanization of silicone rubber compounds was undertaken. It had been found in some earlier work that benzoyl peroxide decomposes very rapidly at a temperature of 200°F. This indicates that the primary vulcanization reaction of silicone rubber with benzoyl peroxide takes place in the press cure, which is usually carried out for 15-30 minutes at 220°F. to 300°F. As a matter of fact, it is only natural to be careless about the time and temperature of press curing because it is the common impression that most of the curing occurs

TABLE XVI

PRESS CURING OF G. E. 81223 STOCK

Sam- ple No.	Time & Temp. ¹ of Press Cure	Physical Properties ²				
		Stress @ 200%	Tensile Strength p.s.i.	Elon- gation Per- cent	Hard- ness Shore A	Comp. ³ Set%
A	5 min. rise to 210°F.	308	743	375	34	25.0
B	10 min. rise to 230°F.	627	764	250	47	37.4
C	10 min. rise to 230°F. 45 min. @ 230°F.	652	842	263	46	47.9
D	10 min. rise to 230°F. 410 min. @ 230°F.	679	839	263	47	45.6
E	10 min. rise to 230°F. 415 min. @ 230°F.	710	932	250	47	46.2
F	10 min. rise to 250°F. 45 min. @ 250°F.	641	914	275	55	57.5
G	10 min. rise to 250°F. 410 min. @ 250°F.	675	763	225	56	56.9
H	10 min. rise to 250°F. 415 min. @ 250°F.	667	758	250	55	56.0
I	15 min. rise to 300°F. 45 min. @ 300°F.	715	715	200	55	56.6
J	15 min. rise to 300°F. 410 min. @ 300°F.	675	675	200	55	58.5

- ¹ Thermometer was placed in platen to measure temperatures.
- ² All slabs, oven-cured, using 48-hr. factory cycle up to 480°F., before measuring physical properties.
- ³ Compression set according to A.S.T.M. D-395-49T (Method B), 22 hours at 300°F.

TABLE XVIII

OVEN CURING OF TITANOX RANC STOCK¹

..(40 VOL. 2.0% BENZOYL PEROXIDE) ..

Sample No.	Time & Temp. of Oven Cure	Physical Properties				
		Stress @ 200%	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	Comp. Set % ²
TA	1 hr. @ 300°F.	720	720	200	53	82
TB	8 hrs. @ 300°F.	---	663	175	55	80.6
TC	8 hrs. @ 300°F. / 16 hrs. @ 400°F.	---	662	175	55	65.5
TD	8 hrs. @ 300°F. / 16 hrs. @ 450°F.	---	607	163	51	63.0
TE	8 hrs. @ 300°F. / 2 hrs. @ 350°F. / 16 hrs. @ 400°F. / 8 hrs. @ 480°F.	---	365	125	52	66.0
TF	8 hrs. @ 300°F. / 2 hrs. @ 350°F. / 16 hrs. @ 400°F. / 8 hrs. @ 480°F. / 5 hrs. @ 400-500°F. / 2 hrs. @ 500°F.	---	600	150	55	55.4

¹Press cure 10 min. rise to 230° / 15 minutes @ 230°F.²Compression set according to A.S.T.M. D-395-49T (Method B), 22 hrs. @ 300°F.

TABLE XVII

OVEN CURING OF GENERAL ELECTRIC 81223¹

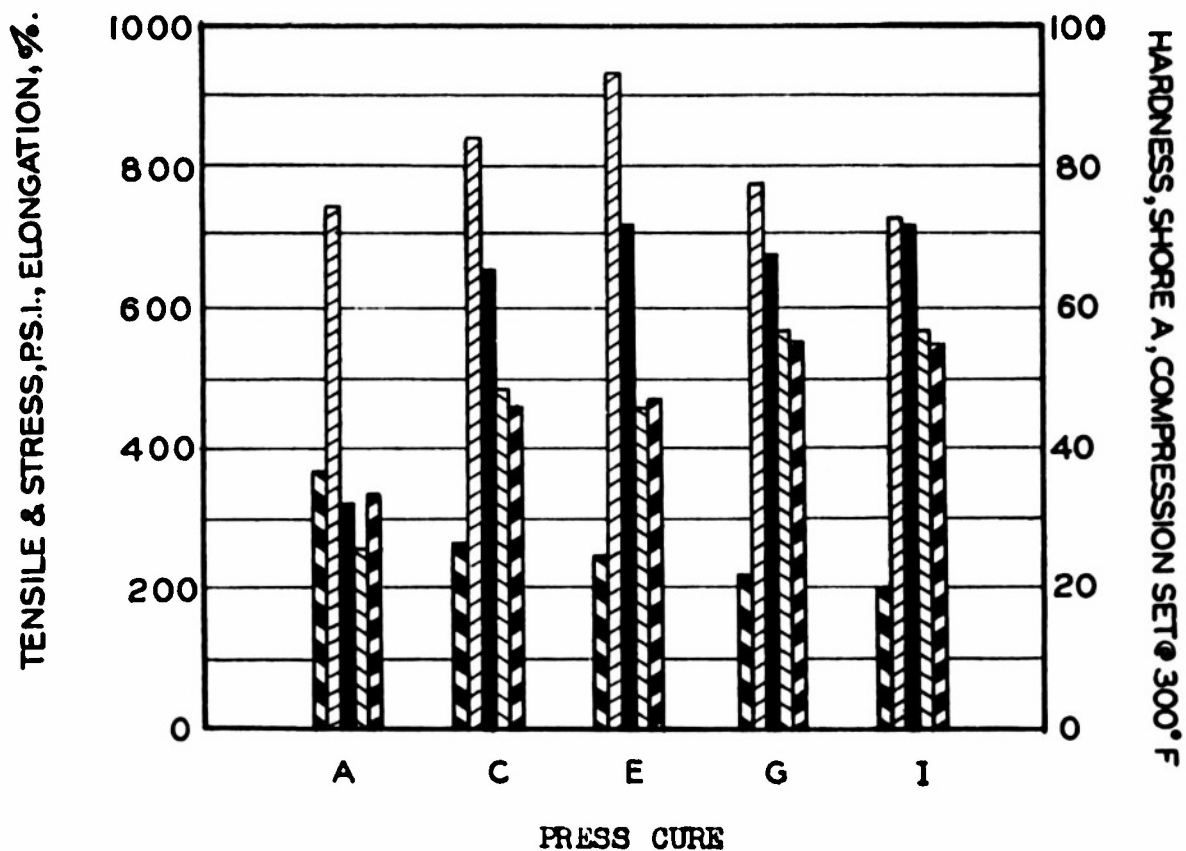
Physical Properties

Sample No.	Time & Temp. of Oven Cure	Stress C 200%	Tensile Strength p.s.i.	Elon- gation Percent	Hard ness- Shore A	Comp. Set % ²
SA	1 hr. @ 300°F.	560	865	275	50	64.3
SB	8 hrs. @ 300°F.	704	933	225	55	58.3
SC	8 hrs. @ 300°F. / 16 hrs. @ 400°F.	729	786	238	55	52.3
SD	8 hrs. @ 300°F. / 16 hrs. @ 450°F.	658	726	225	52	52.1
SE	8 hrs. @ 300°F. / 2 hrs. @ 350°F. / 16 hrs. @ 400°F. / 8 hrs. @ 480°F.	637	699	238	49	59.9
SF	8 hrs. @ 300°F. / 2 hrs. @ 350°F. / 16 hrs. @ 400°F. / 8 hrs. @ 480°F. / 5 hrs. @ 400-500°F. / 2 hrs. @ 500°F.	673	685	213	50	50.3

¹ Press-cure 10 min. rise to 230° / 15 minutes @ 230°F.

² Compression set according to A.S.T.M. D-395-49T (Method B),
22 hrs. @ 300°F.

FIG. II



PRESS CURES

- A 5' RISE TO 210°F.
- C 10' RISE TO 230°F + 5' @ 230°F
- E 10' RISE TO 230°F + 15' @ 230°F
- G 10' RISE TO 250°F + 10' @ 250°F
- I 15' RISE TO 300°F + 5' @ 300°F

LEGEND






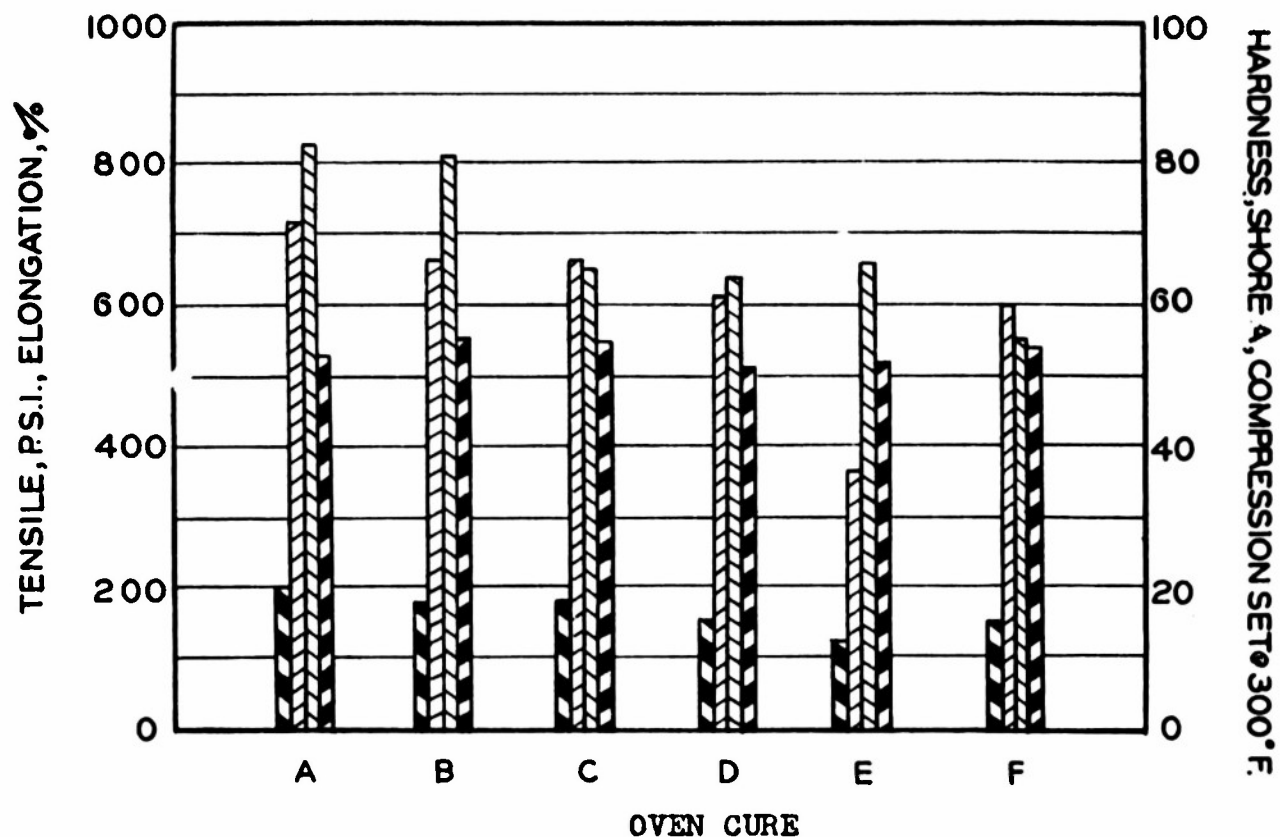
-  TENSILE
-  ELONGATION
-  STRESS @ 200%
-  COMPRESSION SET @ 300°F
-  HARDNESS

FIG. III







PHYSICAL PROPERTIES VS. OVEN CURE
40 VOLUMES TITANOX RANC IN G.E. 81176 GUM
2.0% B.P.

OVEN CURES

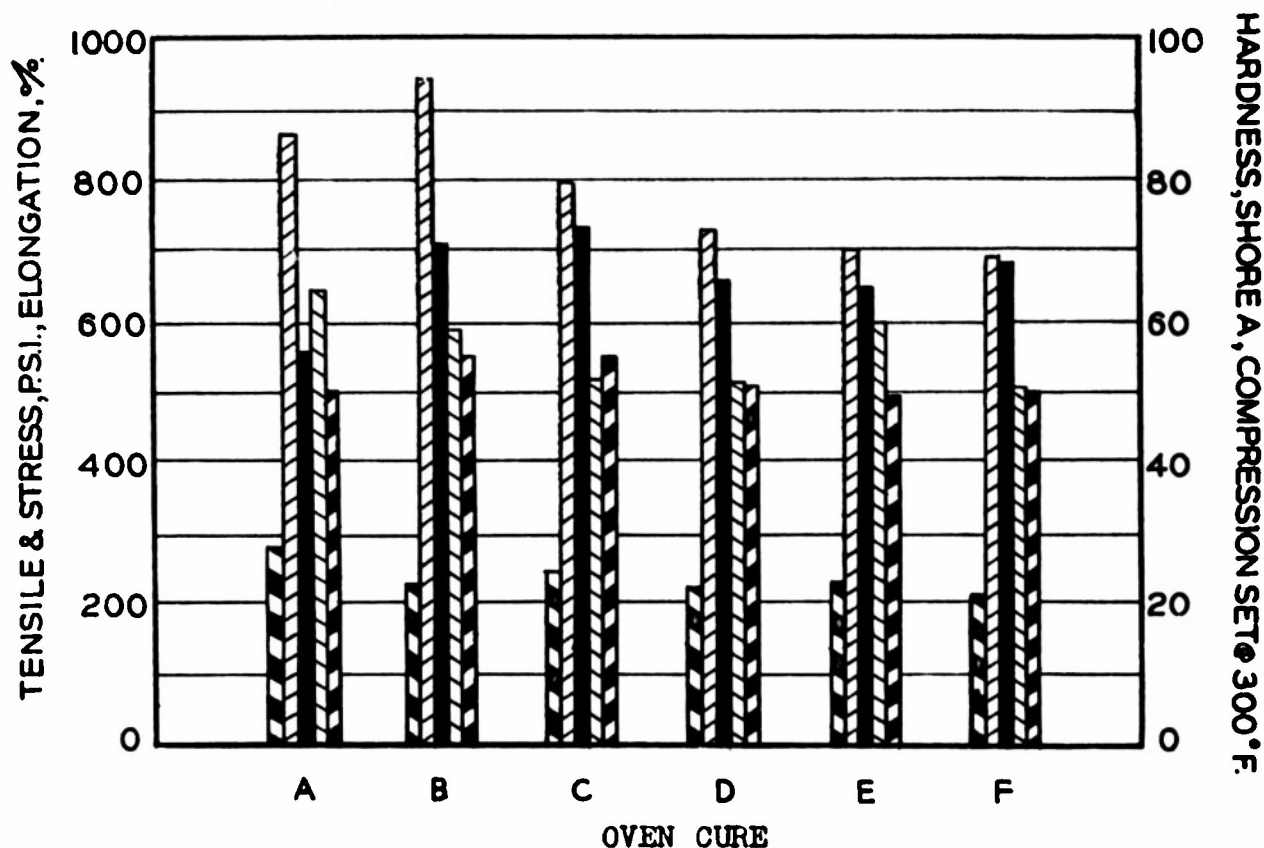
- A 1 HR @ 300°F
- B 8 HRS @ 300°F
- C 8 HRS @ 300°F + 16 HRS @ 400°F
- D 8 HRS @ 300°F + 16 HRS @ 450°F
- E 8 HRS @ 300°F + 2 HRS @ 350°F
16 HRS @ 400°F
8 HRS @ 480°F
- F 8 HRS @ 300°F + 2 HRS @ 350°F
16 HRS @ 400°F
8 HRS @ 480°F
5 HRS @ 400-500°F
2 HRS @ 500°F

LEGEND

-  TENSILE
-  ELONGATION
-  COMPRESSION SET @ 300°F
-  HARDNESS

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U.S. GOVT. CONTRACT DA44-169-qm-64

FIG. IV



PHYSICAL PROPERTIES VS. OVEN CURE
G.E. 81223 SILICONE RUBBER COMPOUND
PRESS CURE: 15' @ 230°F

OVEN CURES

- A 1 HR @ 300°F
- B 8 HRS @ 300°F
- C 8 HRS @ 300°F + 16 HRS @ 400°F
- D 8 HRS @ 300°F + 16 HRS @ 450°F
- E 8 HRS @ 300°F + 2 HRS @ 350°F
16 HRS @ 400°F
8 HRS @ 480°F
- F 8 HRS @ 300°F + 2 HRS @ 350°F
16 HRS @ 400°F
8 HRS @ 480°F
5 HRS @ 400-500°F
2 HRS @ 500°F

LEGEND

- TENSILE
- ELONGATION
- STRESS @ 200 %
- COMPRESSION SET @ 300°F
- HARDNESS

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA44-109-qm-64

during the long oven cure at temperatures of 300° - 400°r. If, however, the primary vulcanization reaction takes place in the press, greater care should be taken with the time and temperature of such cures.

In order to prove this point, a completely mixed compound, General Electric 81223, was divided into several portions, each of which was given a slightly different press cure. After the press cure, all slabs were given a common oven cure. Another portion of the same stock was divided into several portions and all were given the same press cure and then were given progressively longer oven cures. The data are shown in Tables XVI and XVII and in Figures II and IV.

With regard to the press curing study, it was found that a press cure consisting of a 10 minute rise to 230°F., with or without an additional 5 minutes at 230°F., produced a thoroughly cured vulcanizate. In this study, 15 minutes at 230°F. produced the maximum tensile. Curing for 5 minutes at 250°F. resulted in a stock which did not change further as time or temperature was raised. It was interesting to note that minimum time and temperature in press gave the best compression set resistance and also resulted in slightly softer compounds. Since compression set resistance is usually one of the desired properties of silicone rubber, it appears that press cures should be limited as much as possible.

The data obtained on progressively longer and higher-temperature oven cures showed that the maximum tensile strength was achieved in eight hours at 300°F. From this point on, the tensile strengths were lower. A low compression set was reached with eight hours at 300°F. plus 16 hours at 400°F. (This compression set test was run at 300°F. It is likely that an even higher temperature of curing would be desirable for compression sets which might be run at 350°F.) Tables and charts facing this page contain the data.

More work was done later on the press curing temperature of 81223 and was reported in Report No. 13. It was found that press cures of 10 minutes at 210°F. were as satisfactory as those carried out for 10 minutes at 230°F., and provided slightly better compression set resistance. Based on these and other data to be reported later, we feel that there is no reason to carry out press cures with benzoyl peroxide for more than 10 minutes at 210°F., and this is our recommended procedure.

Preheating Pigments with Silicone Rubber

An interesting development which has practical significance for silicone rubber manufacturers or compounders was reported in Report No. 9 under the subject, "Preheating Pigment Master Batches". It will be recalled (page 59) that Alon was found to react with and render

TABLE VII
EFFECT OF PREHEATING ALON-81176 MIXTURES

Vol. Benzoyl Peroxide Alon Percent	Stress @ 200%	Not Preheated			Stress			Preheated		
		Tensile Strength	Long. %	Hardness Shore A	C 200%	Tensile Strength	Long. %	Tensile Strength	Long. %	Hardness Shore A
0	2.0	---	29	150	---	28	150	---	10	---
5	1.6	56	228	775	114	217	350	217	26	---
5	1.8	66	209	563	118	226	350	226	27	---
5	2.0	67	175	475	150	208	275	208	30	---
10	1.8	64	535	1150	170	814	733	814	30	---
10	2.0	62	518	1183	241	534	400	534	33	---
10	3.0	162	702	733	269	415	300	415	37	---
15	2.0	65	265	1150	160	708	833	708	37	---
15	2.5	125	482	875	218	765	625	765	39	---
15	3.0	131	511	950	319	770	475	770	43	---
15	3.5	155	558	850	409	730	350	730	48	---
15	4.0	176	586	675	465	790	363	790	47	---
15	4.5	244	630	600	623	597	188	597	53	---
15	5.0	224	582	650	---	548	150	548	56	---
20	3.0	132	455	783	345	629	442	629	57	---
20	3.5	243	569	550	470	683	375	683	60	---
20	4.0	381	621	413	421	667	375	667	64	---
20	5.0	436	700	408	596	738	288	738	64	---

*porous

Equivalent cures in each section, underlined. Evidence shows preheating is equivalent in effect to an extra 1 to 1.5 percent of benzoyl peroxide.

inactive a substantial proportion of the benzoyl peroxide added to the mixture. In one experiment, benzoyl peroxide was omitted, and the rubber was mixed with Alon and heated before benzoyl peroxide was added. It had been expected that this might tend to depolymerize the rubber to some extent because of the slightly acidic surface of the Alon. After the benzoyl peroxide was added and cures were made and tests obtained, it was found that a definitely stiffer, stronger compound had resulted.

Preheating experiments in the absence of benzoyl peroxide were then carried out on a large number of Alon mixes and on mixes containing other pigments. In the case of Alon, it was found that the preheating treatment caused the rubber to wet the Alon very thoroughly, caused some volatilization of low-molecular-weight silicone rubber and generally raised the modulus, hardness and tensile strength of the preheated compound. It was found that approximately one third of the benzoyl peroxide usually necessary with Alon could be eliminated. Data illustrating this remarkable effect are shown in Table XII, facing this page. It will be noted in this table that as the volume loading of Alon is increased from 5 to 20, it is necessary to add more and more benzoyl peroxide. However, in the mixtures which were preheated for one hour at 300°F., much less benzoyl peroxide was necessary to reach a given state of cure than for those batches which were not

TABLE XX

EFFECT OF PREHEATING, USING PIGMENTS OTHER THAN ALON

Pigment and Vol. Loading	Preheat	Stress @ 200%	Tensile Strength	Elongation Percent	Hardness Shore A
Hi-Sil 15	No	217	261	283	37
	Yes	354	456	258	40
Santocel C 15	No	387	737	383	52
	Yes	676	826	275	56
Witcarb F 40	No	159	252	700	32
	Yes	137	177	458	34
Titanox FANC 40	No	197	484	417	41
	Yes	507	581	267	45
Celite Super Floss 40	No	456	465	208	58
	Yes	---	497	150	66
Celite Super Floss 40	No	---	472	175	60
	Yes	---	495	150	68
	No*	---	478	175	56

* Gum alone was preheated 1 hour at 300°F., then directly mixed with pigment and curative.

preheated.

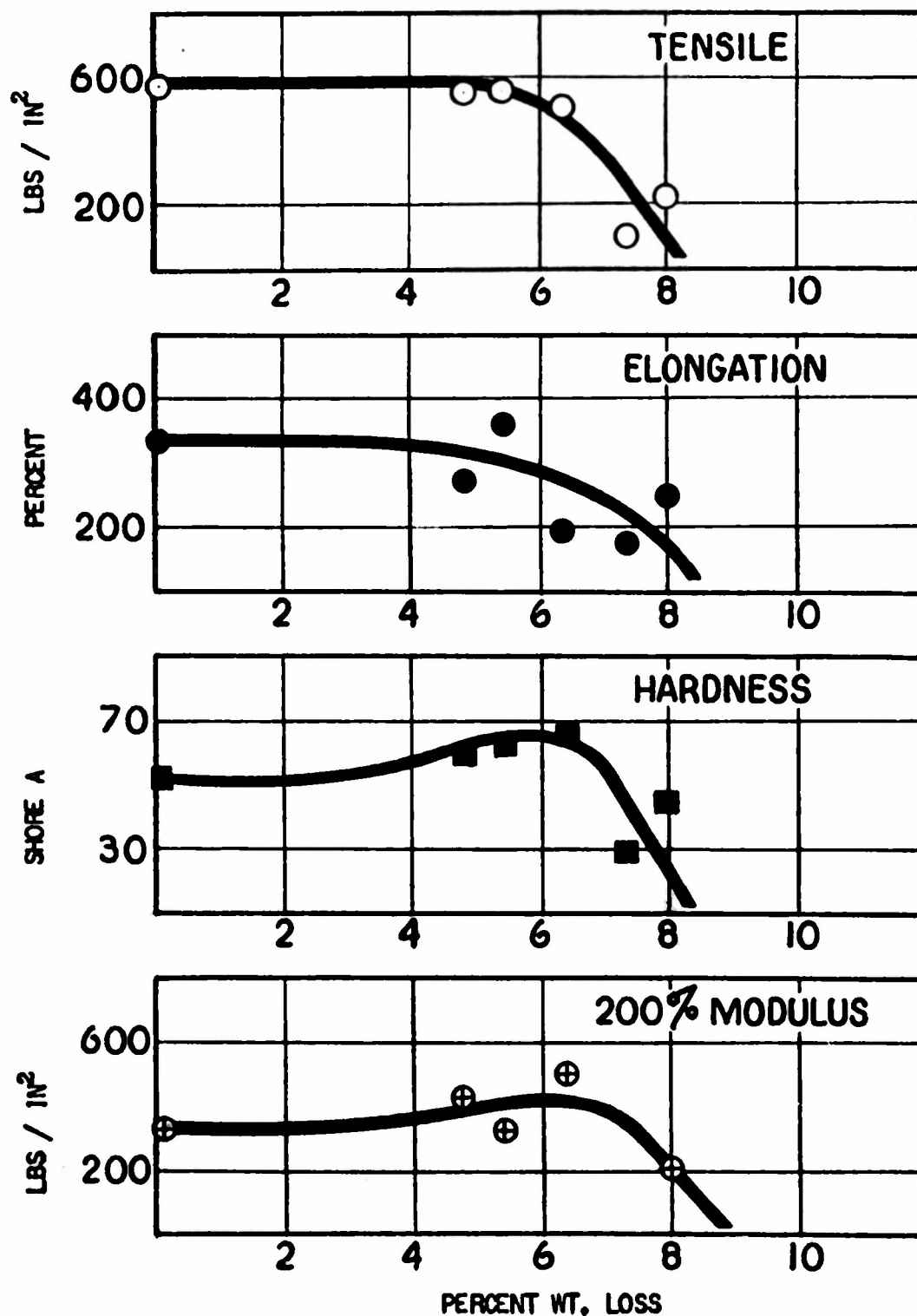
In Table IX, facing this page, the effect of the one hour at 300°F. preheating treatment upon physical tests obtained with five other reinforcing agents is shown. The preheating treatment is shown to have a beneficial effect as far as reinforcement is concerned with Hi-Sil, Santocel C, Titanox RMC and Celite Super Floss. With Witcarb R, there appeared to be no beneficial effect.

Summarizing the advantages of this refinement on the mixing process, it may be said that preheating promotes evaporation of low-molecular-weight silicone oils which are of little value in the final product. Preheating, therefore, causes a reduction in shrinkage during oven curing. Preheating makes it possible to reduce the benzoyl peroxide concentration and results in higher tensile strength and higher modulus stocks. There was some indication that preheating resulted in a slight improvement in compression set resistance. A study of different times and temperatures of preheating indicated that there was little to be gained by increasing the time of preheating beyond one hour at 300°F.

Moisture on Fillers

During the study of the advantages of preheating, it was suggested that part of the benefits might come from removal of surface moisture on the pigments during the

FIG. V



**PHYSICAL PROPERTIES VS. WT. LOSS OF PIGMENT
ON HEATING AT 200°-1700°F.**

SANTODOL-C IN 81176 SILICONE GUM. 15 VOLUMES 2.0% B.P.

TABLE XXI

SANTOCCEL C WITH VARYING WATER CONTENT¹

Sample No.	Time & Temp. of Heating (OF.)	Pigment Wt. Loss (%)	Pigment ³ pH (H ₂ O)	Compd. No.	Physical Properties ²		
					Stress @ 200%	Tensile Strength p.s.i.	Elongation Percent
S-88	Not heated	---	3.88	1993	333	576	338
S-89	6 Hrs. @ 220°	5.40	3.86	1993-1	367	577	325
S-90	4 Hrs. @ 500°	4.82	3.85	1993-2	421	559	275
S-91	3 Hrs. @ 1000°	6.38	4.23	1993-3	506	506	200
S-92	3 Hrs. @ 1500°	8.00	6.20	1993-4	202	234	250
S-93	1 Hr. @ 1700°	7.35	8.17	1993-5	---	101	175

¹Compounded with G.E. 81176 silicone gum, 15 vols. per 100 vols. gum, 2.0% benzoyl peroxide

²Press cure, 15 minutes @ 250°F. Oven cure 1 hour @ 300°F.

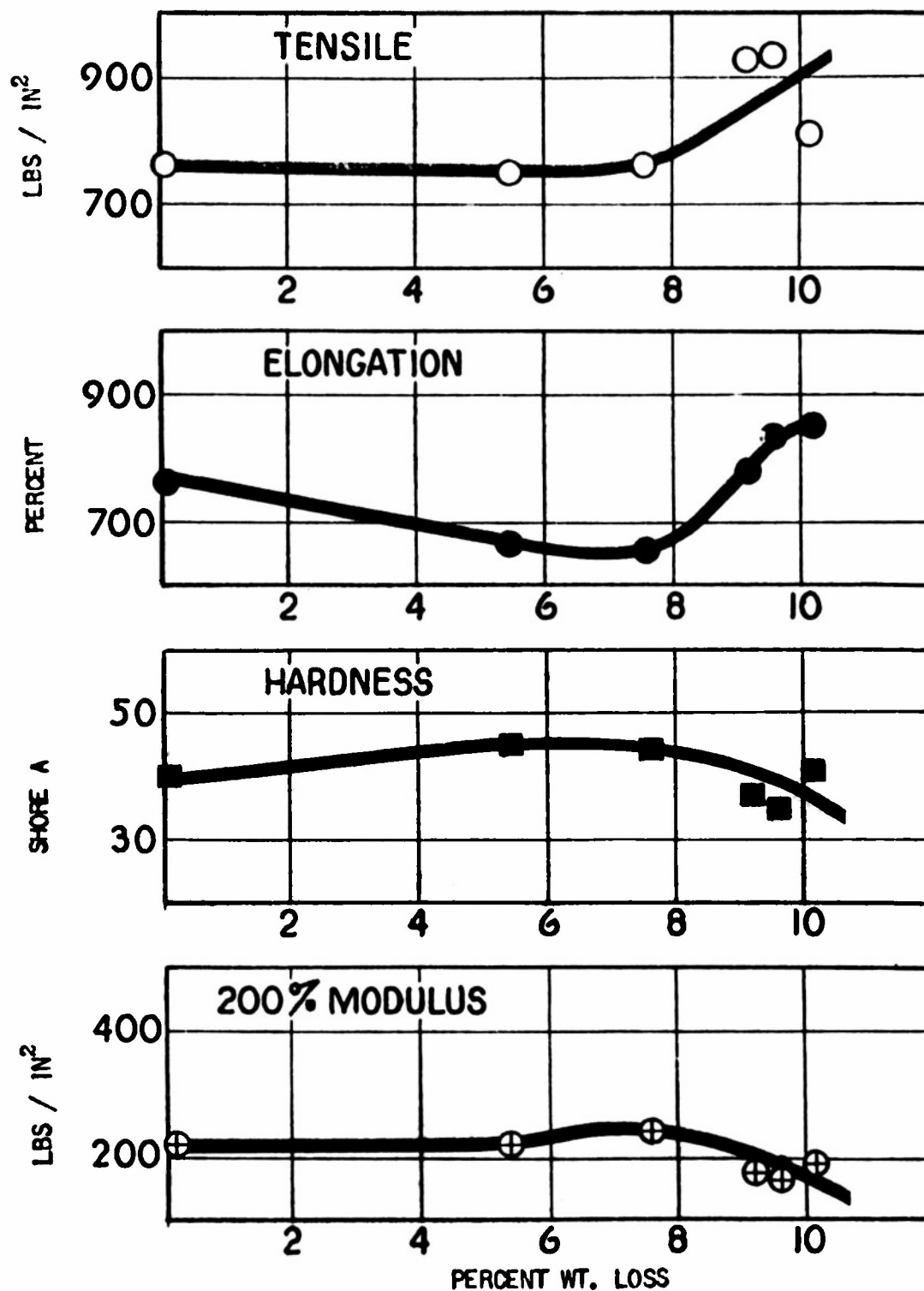
³pH of 0.5 gms. pigment in 25 ml. boiled distilled water (pH 6.8 - 7.0)

preheating treatment. It was therefore decided to study the effect of direct removal of moisture on the surface of pigments to see if any improvement in reinforcement would be obtained. In order to accomplish this, a sample of Santocel, which is very hygroscopic, and a sample of Alon were exposed for twenty-four hours to saturated water vapor at room temperature. They were then heated for several hours at several different temperatures to remove water to a varying degree. The samples were then tested in SE-76 rubber, as shown in Table XXI and Figure V, facing this page, and in Table XXII and Figure VI facing the next page.

With Santocel C, the heating caused the pigment to lose as much as 8 percent in weight, and the pigment surface became more alkaline, reaching a pH of 8.2. Reinforcement was increased by all of the heating periods up to and including three hours at 1000°F. At temperatures above 1000°F., the pigment sintered and lost most of its reinforcing qualities.

The Alon sample lost moisture up to 10.19 percent, and its pH increased to 7.85. Reinforcement, as measured by the increased modulus, increased up to a period of heating of three hours at 500°F. It was interesting to note that heating Alon at 1500° and 1700°F. brought it far over on the alkaline side and although it was then less strongly reinforcing, it gave the highest tensile

FIG. VI



**PHYSICAL PROPERTIES VS. WT. LOSS OF PIGMENT
ON HEATING AT 200°-1700°F.**

ALON IN 81176 SILICONE GUM, 15 VOLUMES, 4.0% B.P.

TABLE XXII

ALON WITH VARYING WATER CONTENT¹Physical Properties²

Sample No.	Time & Temp. of Heating (°F.)	Wt. Loss (%)	Pigment ³ pH (H ₂ O)	Compd. No.	Stress @ 200%	Stress @ 400%	Tensile Strength @ p.s.i.	Elongation Percent	Hardness Shore A
S-99	Not heated	---	5.05	1994	206	439	767	763	40
S-100	5 Hrs. @ 220°	5.48	4.92	1994-1	220	433	751	663	45
S-101	3 Hrs. @ 500°	7.61	5.76	1994-2	245	503	763	650	45
S-102	2 Hrs. @ 1000°	10.19	5.70	1994-3	189	405	810	850	41
S-103	3 Hrs. @ 1500°	9.60	7.85	1994-4	164	416	938	838	35
S-104	1 Hr. @ 1700°	9.19	7.80	1994-5	171	428	925	775	37

¹Compounded with G.E. 81176 silicone gum, 15 vols. per 100 vols. gum, 4.0% benzoyl peroxide

²Press cure 15 minutes @ 250°F. Oven cure 1 hour @ 300°F.

³pH of 0.5 gms. pigment in 25 ml. boiled distilled water (pH 6.8 - 7.0)

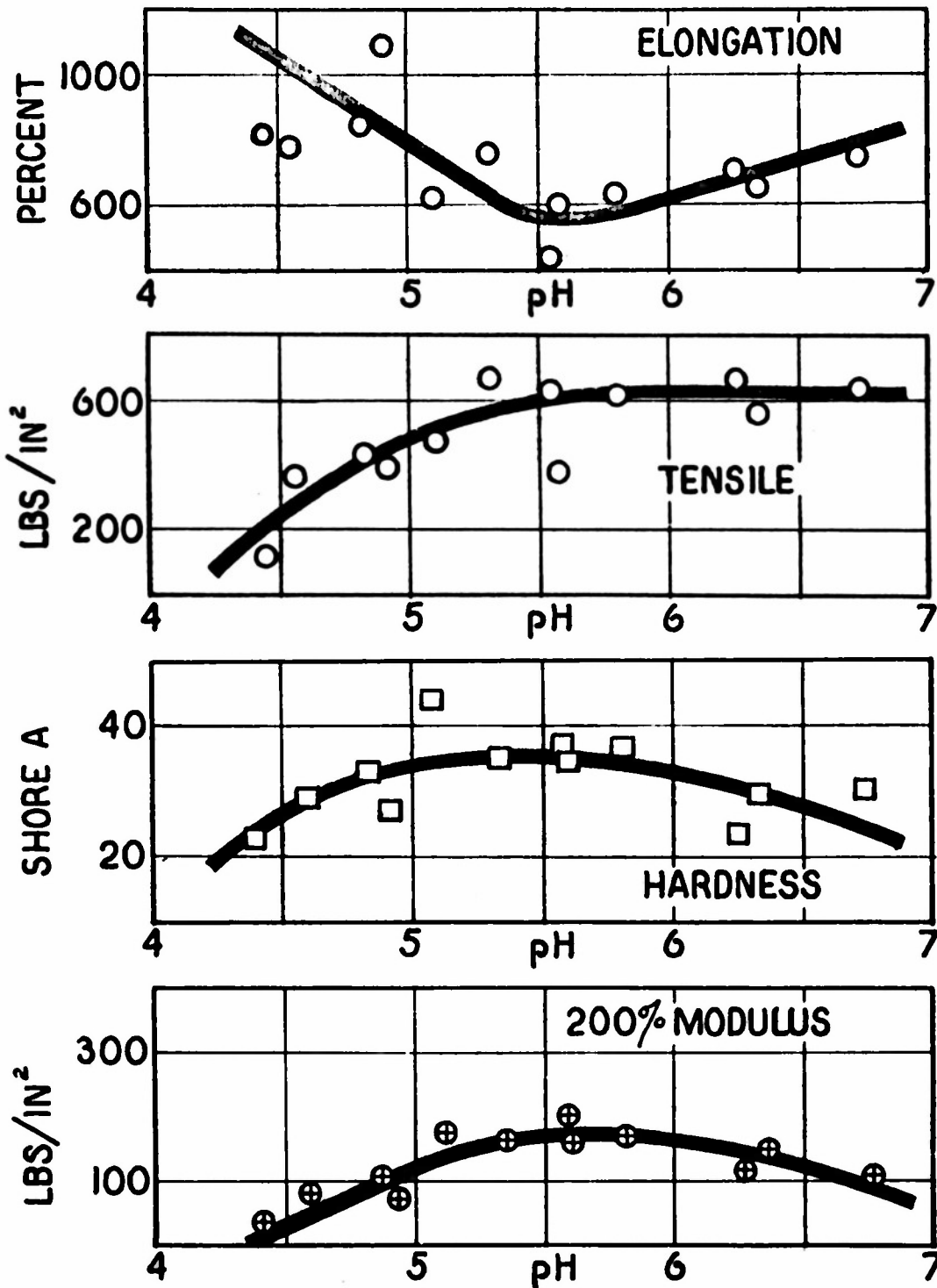
strengths. Since Alon is produced by an acid process involving hydrochloric acid and the last step in its preparation is the removal of this acid by heating, it appears that an even greater amount of heating of the Alon might be beneficial if it is to be used to produce high-strength silicone rubber.

In several other miscellaneous experiments where various pigments were heated for 16 hours at 500°F. in order to remove all traces of water from their surfaces, improved reinforcement was obtained in several cases and notably in one case, Titanox RANC. We feel that surface moisture is undesirable but that the preheating treatment of rubber and pigment together has other advantages in addition to removing moisture on the surface of the pigment.

pH of Surface of Reinforcing Fillers

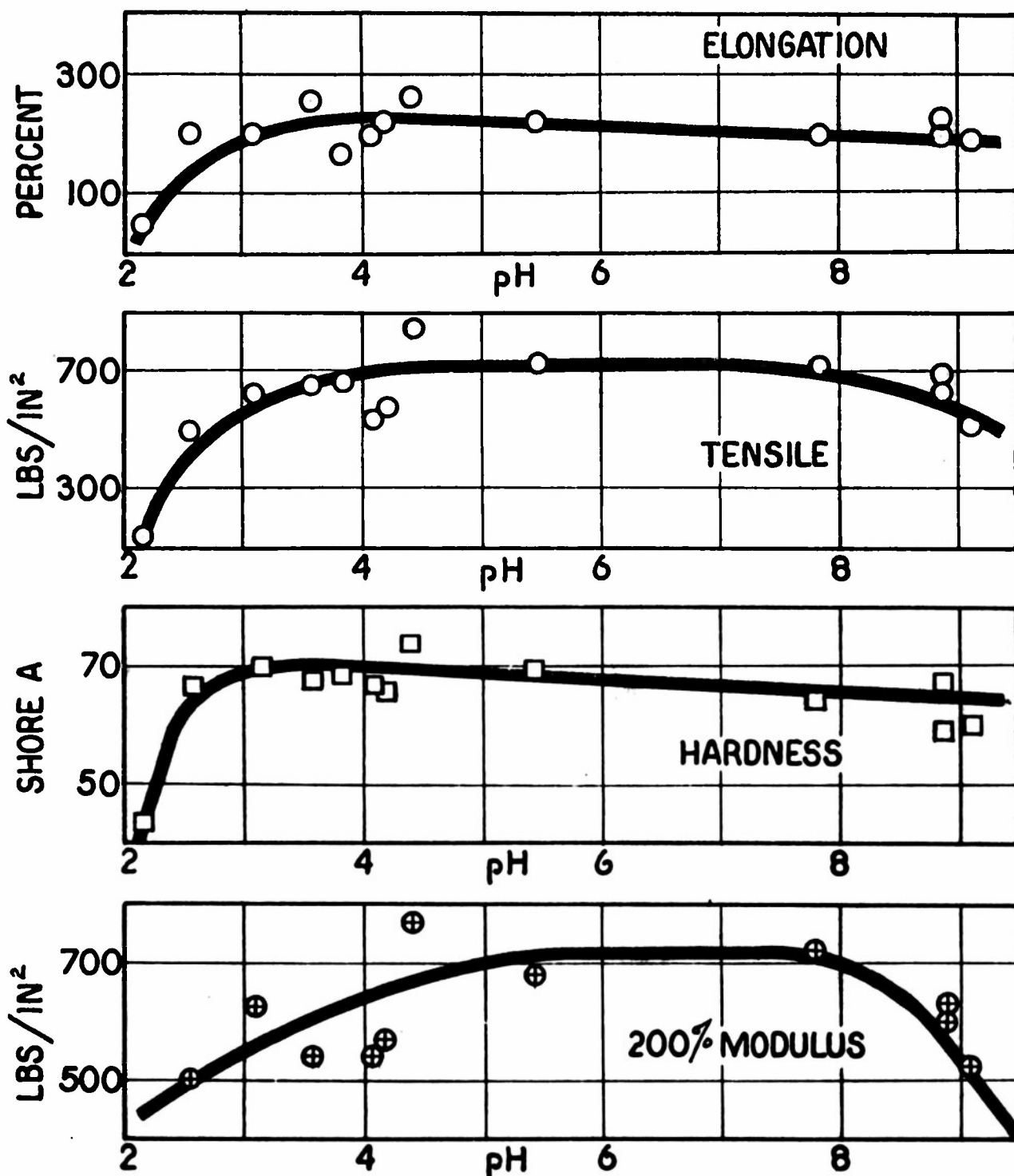
Because Alon and Santocel C are both slightly acidic, it was thought that the acidity or alkalinity of the surface of a pigment might show some relationship to its reinforcing value. In order to investigate this matter, Alon, Santocel C and titanium dioxide were treated with hydrogen chloride gas, on the one hand, and with ammonia gas, on the other. The excess gas was removed in various ways: by heating at varying temperatures and by heating in vacuum. The pH of the treated pigment was determined by suspending 0.5 gram quantities of the pigment in 100 cc.

FIG. VII



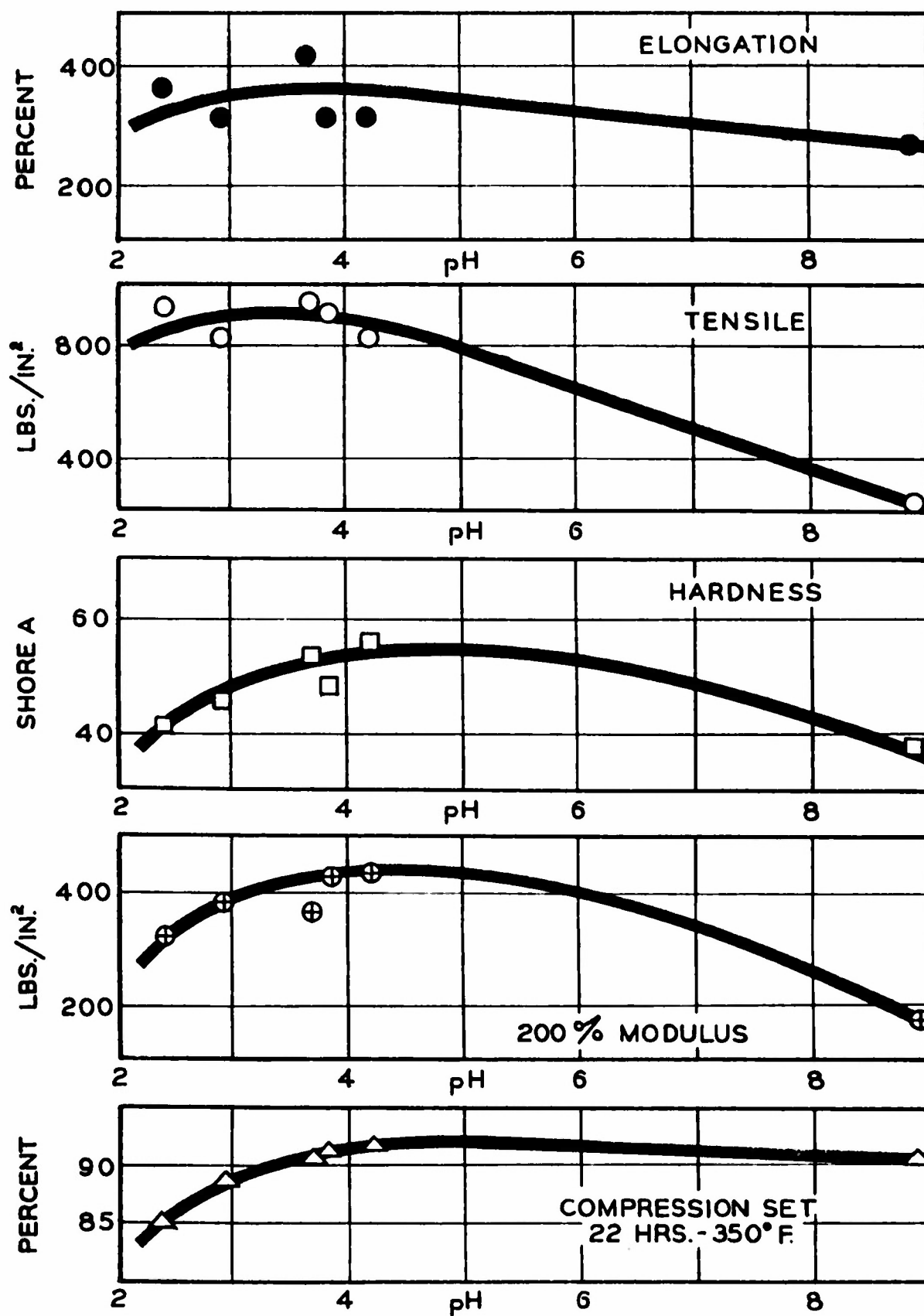
PHYSICAL PROPERTIES vs. pH OF PIGMENT
ALON IN 81176 SILICONE GUM - 10 VOLUMES 4.0% B.P.

FIG. VIII



PHYSICAL PROPERTIES vs. pH OF PIGMENT
 SANTOCCEL-C IN 81176 SILICONE GUM - 16.6 VOLUMES, 4.0% B.P.

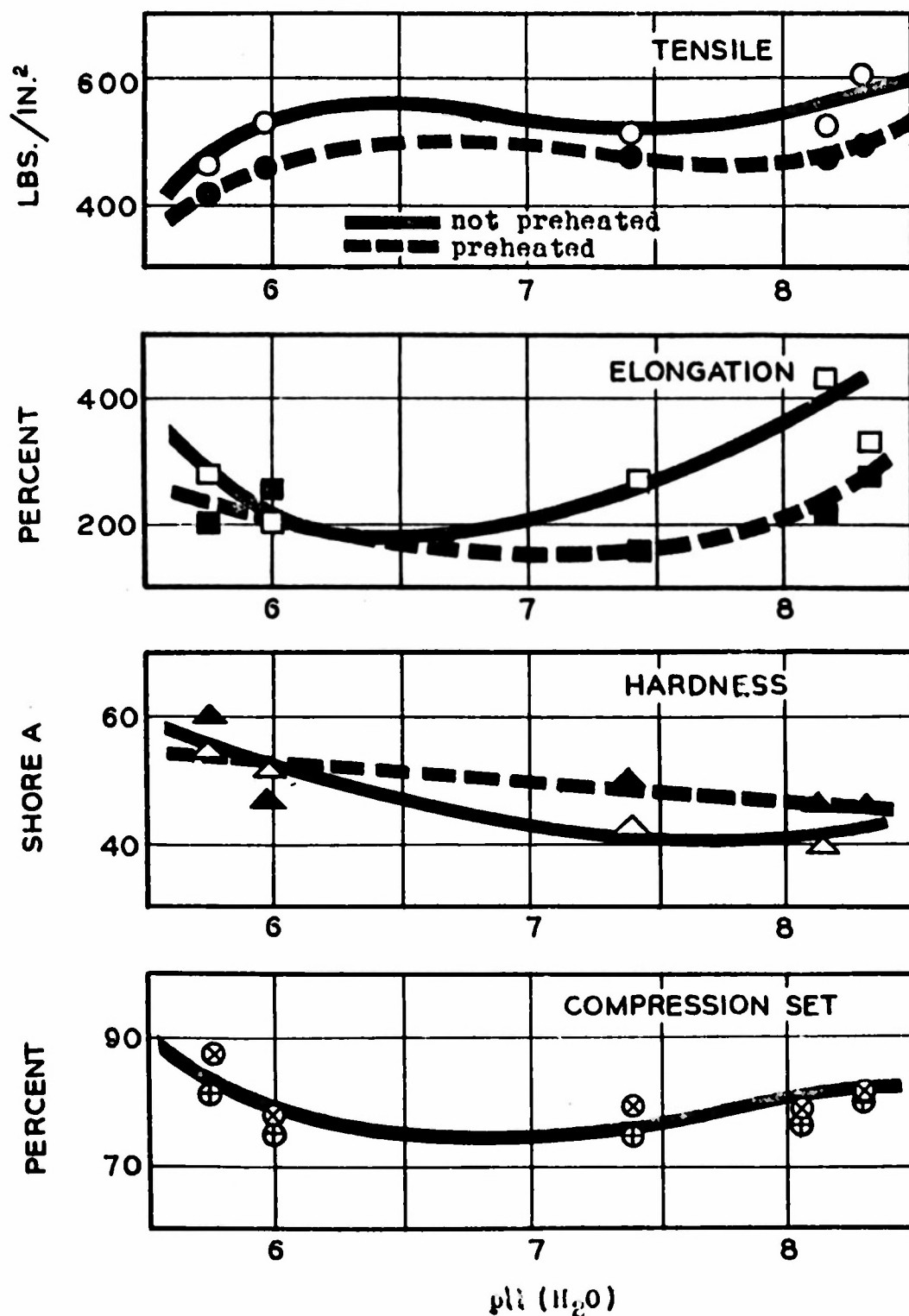
FIG. IX



PHYSICAL PROPERTIES VS. pH OF PIGMENT
SANTOCCEL C IN 81175 SILICONE GUM - 15 VOLS., 2.0% B.P.

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA14-109-qm-64

FIG. X



PHYSICAL PROPERTIES VS. pH OF PIGMENT
 TITANOX RANC IN G.E. 81176 SILICONE GUM
 40 VOLIS., 2.0% B.P.

of water and determining the pH of the suspension. Interesting results were obtained which are shown graphically in Figures VII, VIII, IX and X, facing this page.

With Alon maximum reinforcement appears to be obtained at a pH of approximately 5.5, with modulus and hardness falling off on either side of this point. The elongation is a minimum at this point, indicating that either acidic or alkaline surfaces of Alon result in higher elongation test results.

With Santocel C, the range at which good reinforcement is obtained is broader than with Alon and extends from a pH of approximately 3 to 8. Excess acid on the low pH side or excess alkali on the high pH side causes all properties to fall off. This broader range of utility with Santocel C may be associated with the high absorptive nature of this pigment. It is possible that Santocel C has capacity to absorb and render harmless a considerable quantity of acid or alkali.

The results with titanium dioxide were less conclusive than those with Alon and Santocel C. It appears from the data that titanium dioxide with a pH between 6 and 8 will give satisfactory reinforcement.

Coating Pigments with Silicone Oils to Improve Reinforcement

Work has already been reviewed on early attempts to improve reinforcement obtained with fillers in SE-79 rubber

TABLE CIII

SAITOCCEL C - 20 VOLUMES COATED WITH SILICONE OILS IN SE-76 RUBBER

Coating	Cure	Percent by weight	Stress @ 200 percent	Tensile		Elongation Percent	Hardness Shore A	Reference Report No.
				Strength p.s.i.	Strength p.s.i.			
None	1 hr. @ 300°F.	0	475	669		238	72	10 p.33
CCl ₄ only	"	0	635	635		200	70	"
G.E.998ILT-4	"	10	498	703		300	65	"
"	"	100	319	1025		500	60	"
NH ₃ -stab.oil	"	1	468	612		263	68	"
"	"	10	718	1000		275	65	"
"	"	100	-	740		100	85	"
G.E.998ILT-4	1 hr. @ 300°F.	1	297	643		250	70	12 p.32
"	16 hrs. @ 480°F.		403	540		150	74	"
"	1 hr. @ 300°F.	10	229	1000		400	63	"
"	16 hrs. @ 480°F.		413	468		150	72	"
"	1 hr. @ 300°F.	20	259	976		325	66	"
"	16 hrs. @ 480°F.		459	560		125	76	"
"	1 hr. @ 300°F.	40	234	902		350	62	"
"	16 hrs. @ 480°F.		413	716		200	73	"
"	1 hr. @ 300°F.	60	189	757		350	50	"
"	16 hrs. @ 480°F.		334	680		225	66	"
"	1 hr. @ 300°F.	80	162	838		450	47	"
"	16 hrs. @ 480°F.		292	541		200	60	"

TABLE XXIII (cont.)

SANTOCEL C - 20 VOLUMES COATED WITH SILICONE OILS IN SD-76 RUBBER

Coating	Cure	Percent by weight	Stress @ 200 percent	Tensile		Elongation Percent	Hardness Shore A	Reference Report No.
				Strength p.s.i.	Strength p.s.i.			
G.E. 9981LT-4 "	1 hr. @ 300°F.	100	117 260	656	614	525	43	12 p.32 "
	16 hrs. @ 480°F.					233	61	

NOTE: All cures contained 2 per cent benzoyl peroxide based on total amount of silicone rubber and oil present and were press cured for 15 minutes at 2300F. Percentage of SD-76 was reduced as silicone oil was increased.

by coating them with silicone oils. Very little beneficial effect was noted. It seemed wise to investigate again the possibility that silicone oils placed in intimate contact with pigments might improve the bond obtained between filler and rubber. For the purpose, Santocel C was selected for preliminary work because it is known to possess a considerable pore structure; thus large amounts of oil could be added to the pigment. The technique used was to dry the pigment by heating for several hours at 500°F. to remove the moisture. The selected amount of oil was dissolved in carbon tetrachloride and added to the pigment. Carbon tetrachloride reduces the viscosity of the silicone oil solution so that it can penetrate and coat the fine particles easily. The carbon tetrachloride was evaporated in an oven at 200°F. Table XXIII, facing this page, shows the results of a study of various amounts of oils on Santocel C in 20-volume loadings in SE-76. Most of the work was done with General Electric 9981LT-4 silicone oil. It was observed that as the amount of oil on the surface of the pigment was increased up to 100 per cent by weight, the modulus and hardness decreased while the elongation and tensile strength increased. This appears to be true for oven cures of one hour at 300°F., or 16 hours at 480°F. Precautions were taken to increase the benzoyl peroxide in proportion to the additional silicone material present in the recipe. Furthermore, the amount of rubber was

decreased as the silicone oil was increased, so that the 20-volume loading of Santocel C remained constant, based on the total amount of silicone material present.

Ammonia-stabilized liquid gum was used in the same manner as the silicone oil. This material was found to result in an increase in modulus and hardness as the percentage was increased.

When the General Electric 2981LT-4 oil was used with Hi-Sil, Spheron 6 and Titanox RMC, the effects were much less apparent, indicating that the capacity of the Santocel C for absorbing the oil has a lot to do with the results obtained.

It was concluded that compounds made with Santocel C could be modified considerably with the use of this technique.

The Linde Air Products Company has proposed the use of alkyl trichlorosilanes as coating materials for pigments. After the addition of silane to the pigment it is exposed to water vapor which hydrolyzes the chlorine atoms, and the silanols are condensed to form a siloxane coating on the surface of the pigment. This treatment was tried with methyl trichlorosilane, vinyl trichlorosilane and dimethyl dichlorosilane on the surface of Santocel C, Titanox RMC, Celite 800 and Spheron 6. In all but one of these cases, no outstanding improvements were observed over the normal reinforcement afforded by the uncoated

pigment. The exception was Spheron 6, in which case a vinyl siloxane coating seemed to increase the stiffness, hardness and tensile strength of the compound in which the coated carbon black was used. The maximum tensile strength was 400 p.s.i. Further work might very profitably be done with carbon black and siloxane coatings.

Molecular Weight of SE-76 Silicone Rubber

In connection with the work on GS199S Silica, it was found desirable to measure the molecular weight of the SE-76 that was being used with the GS199S Silica. A careful study was made of all of the samples of SE-76 rubber which had been used during the past six years. The average molecular weights of these samples were arrived at by determining the limiting solution viscosity at infinite dilution. The use of this result in the Staudinger equation relating viscosity and molecular weight enabled us to arrive at the molecular weights of the various rubbers. In doing this, assistance was gained from work done by Flory and his collaborators, which provided values for the constants in the Staudinger equation. Three pages reporting this work are reproduced here from Report No. 13.

Note on Molecular Weight of Silicone Polymers

"Molecular weights of the various batches of SE-76 polymer were determined from viscosity data of dilute

solutions, using the method used by Flory et al (1).

"Dilute solutions of each polymer were made at several concentrations in methyl ethyl ketone. Their viscosity was determined at 26°C., using a standard Ostwald viscometer, and values for $[\eta]_{\infty}$ MEK at 26°C. were determined for infinite dilution by extrapolation.

"These data were then applied to the Staudinger equation:

$$[\eta] = KM^a \quad (1)$$

where M is the molecular weight, and K and a are constants for a given polymer - solvent system at one temperature.

"In order to find the values of these constants, the data of Flory et al (1) were used. Flory determined the limiting viscosity, $[\eta]_{\infty}$ MEK, values for polydimethylsiloxane fractions of known osmometric molecular weights at 20° and 30°C. in methyl ethyl ketone. From a plot of eq.(1) in the form:

$$\log [\eta] = \log K + a \log M \quad (2)$$

the constants K and a were determined for 20° and 30° C.

"Flory's data for $[\eta]_{\infty}$ MEK at 20° and 30°C. were re-plotted using the Arrhenius equation:

$$[\eta] = Ae^{-B/T} \quad (3)$$

to obtain values of $[\eta]_{\infty}$ at 26°C. for the fractions of known osmometric molecular weight. A third plot of equation (2)

(1) Flory, P.J., et al, J.Am.Chem.Soc. 74,3364 (1952)

was then made to give constants K and a at 26°C. Values of M from our data at 26°C. could then either be read off the plot or calculated with the 26° constants.

"Values for the Staudinger equation constants for polydimethylsiloxane in methyl ethyl ketone are as follows:

TABLE XXIV

STAUDINGER EQUATION CONSTANTS FROM FLORY'S DATA

<u>Temp. °C.</u>	<u>Kx10³</u>	<u>log K</u>	<u>a</u>
20°	0.80	-3.099	0.50
26°	0.66	-3.178	0.52
30°	0.55	-3.255	0.54

"The average molecular weights of the various batches of SE-76 from the limiting viscosity at 26°C. are given below:

TABLE XXV

AVERAGE MOLECULAR WEIGHTS FROM VISCOMETRIC DATA

<u>Batch No.</u>	<u>η_{sp}/c</u> <u>MEK 26°C</u>	<u>Molecular Weight</u>
81339	0.820	840,000
4B-5946	0.760	730,000
8826	0.750	710,000
BN-2600	0.632	512,000
B-7155	0.615	483,000
11317(as recd)	0.584	433,000
Fractionated sample:		
11317(high fract)	0.715	643,000
11317(media ")	0.568	408,000
11317(low ")	0.522	352,000 "

TABLE CXVI

VARIOUS BATCHES OF SE-76 AND SANTOCEL C

No.	Batch No.	Mol. Wt.	Pigment	Vol. %	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	Stress @ 200%
2228-1	(A) B-5946	730,000	Santocel C	15	1 hr. @ 300°F.	835	325	51	485
	(B)				24 hrs. @ 300°F.	605	300	56	580
	(C)				24 hrs. @ 400°F.	595	237	50	520
2237-2	(A) 81339	840,000	Santocel C	15	24 hrs. @ 300°F.	870	362	50	390
	(B)				16 hrs. @ 400°F.	815	287	55	435
	(C)				24 hrs. @ 400°F.	580	275	55	415
2401-1	(A) 7155	483,000	Santocel C	15	1 hr. @ 300°F.	891	287	51	590
	(B)				24 hrs. @ 300°F.	708	200	56	668
	(C)				24 hrs. @ 400°F.	650	200	51	650
2228	(A) 11317	433,000	Santocel C	15	1 hr. @ 300°F.	947	425	36	309
	(B)				24 hrs. @ 300°F.	775	350	38	383
	(C)				24 hrs. @ 400°F.	834	325	42	438

Footnotes:

- (1) Gen. Elec. SE-76 gum (different batches) with 2.0% benzoyl peroxide as a curing agent
 (2) Press cure 15 minutes at 230°F., oven cure as indicated

The effect of the average molecular weights given in the above table on the physical properties obtained with the respective rubbers is of considerable interest. We first became conscious of the variation when, after having used Batch No. B-5946 for several months, we were suddenly confronted with Batch No. 11317.

SE-76 of Varying Molecular Weight with Santocel C

As given in Table XXV, the average molecular weights of various batches of SE-76 varied from 433,000 to 840,000. Batch No. B-5946, with which most of our work in 1951 and early 1952 was carried out, had an average molecular weight of 730,000, while Batch No. 11317, which was used during the latter part of 1952, had the lowest average molecular weight, 433,000. This is about fifty percent lower and was a deliberate change in the polymer to impart better plasticity or workability to silicone compounds,

There is no great variation in properties of a standard 15-volume Santocel C stock, cured with benzoyl peroxide, as the molecular weight of the gum is changed. Data are given in Table XXVI. Elongation and low hardness appear to be preserved during high-temperature cures in the lower molecular weight gum.

The only batch of rubber in Table XXVI which appears different from the others is No. 11317. Upon checking with the supplier, we learned that this batch was indeed

TABLE XXVII

FRACTIONATED SE-76 (11317-5) AND 25 VOL% GS199S SILICA

Compound No.	Batch No.	Mol. Wt.	Pigment	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	Stress @ 200%	Stress @ 400%
Average Values	11317-5 (Control) (Not fractionated)	430,000	GS199S	1 hr. 24 " 24 " 16 "	@ 300°F. @ 300°F. @ 400°F. @ 480°F.	860 760 230 <25	52 63 81 88	80 200 540 ---	100 310 880 ---
2414-1 (A) Low Mol. Wt. (B) Fraction		350,000	"	24 " 24 "	@ 300°F. @ 400°F.	707 495	65 81	256 ---	440 ---
2414-2 (A) Medium Mol. Wt. (B) Fraction		410,000	"	24 " 24 "	@ 300°F. @ 400°F.	825 680	66 80	230 ---	423 ---
2414-3 (A) High Mol. Wt. (B) Fraction		640,000	"	24 " 24 "	@ 300°F. @ 400°F.	1030 730	66 80	252 730	445 ---

Footnotes:

- (1) Gen. Elec. SE-76 gum used; fractionated as indicated. No benzoyl peroxide
 (2) Press cure 15 minutes at 230°F.; oven cure as indicated

on the lower limit of their viscosity specification. The supplier claims that there is little effect of the molecular weight of the rubber upon the tensile strength properties above a molecular weight of 300,000. It seems quite possible that Batch No. 11317 contained a substantial portion of rubber of molecular weight less than 300,000. As will be seen below, the molecular weight of the rubber plays a more important part in recipes containing GS199S Silica.

SE-76 of Varying Molecular Weight with GS199S Silica

GS199S Silica will be discussed in greater detail in the section to follow. The effect of the molecular weight of the rubber upon the tensile strength properties obtained with GS199S will, however, be discussed here. As will be shown later, benzoyl peroxide may be omitted completely from recipes containing GS199S as a filler. In other words, the GS199S has the property of vulcanizing the rubber as well as reinforcing it. In the recipes on which data are presented in Tables XXVII, XXVIII and XXIX and Figure XI, no benzoyl peroxide was used. With GS199S Silica reinforcement and cure, better tensile strength is obtained with higher molecular weight polymer.

It was found (Report No. 12) that tensile strengths of over 1000 p.s.i. could not be obtained with Batch No. 11317 gum, whereas tensile strengths of almost 2000 p.s.i. had been obtained with Batch No. 5946. This was traced

TABLE XXVIII

VARIOUS BATCHES OF SE-76 AND 25 VOL% GS199S SILICA

Compound No.	Batch No.	Mol. Wt.	Pigment	Oven Cure	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	Stress @ 200'	Stress @ 400%
Average Values	B-5946	730,000	GS199S	1 hr. 24 " 16 " 24 " 6 "	1140 1530 1320 1210 Brittle	1030 820 500 440 425	57 59 80 80 90	140 250 540 600 ---	210 460 970 940 ---
2372-2 (A) (B) (C) (D)	BK-2600	510,000	GS199S	1 " 24 " 16 " 16 "	286 729 765 Brittle	825 700 400	52 67 77 94	92 201 450 ---	137 331 765 ---
2401-2 (A) (B) (C) (D)	7155	480,000	GS199S	1 " 24 " 24 " 16 "	1281 1605 765 Brittle	825 662 162	62 70 86 88	230 326 --- ---	--- --- --- ---
2413-2 (A) (B) (C) (D) (E)	8826	710,000	GS199S	24 " 2.5 " 18 " 16 " 16 "	1770 1205 1000 1000 141	737 625 425 325 25	65 60 72 76 90	275 301 465 675 Brittle	600 603 928 --- ---
Average Values	11317-5	430,000	GS199S	1 " 24 " 16 " 24 " 6 "	240 670 790 740 Brittle	860 760 420 230 25	52 63 78 81 88	80 200 460 540 ---	100 310 640 880 ---

Footnotes

- (1) Gen. Elec. SE-76 gum used; various batches as indicated
 (2) Press cure 15 minutes at 230°F.; oven cure as indicated

TABLE XVI

VARIOUS BATCHES OF SD-76 AND 15 VOL% GS1993 SILICA

Compound No.	Batch No.	Mol. Wt.	Pigment	Oven Cure	Tensile		Elongation Percent	Hardness Shore A	Stress @ 200%	Stress @ 400%
					hrs.	Strength p.s.i.				
Average Values	R-5946	730,000	GS1993	24	hrs. @ 300°F.	1550	930	47	180	310
				16	" @ 400°F.	1360	740	59	290	520
				24	" @ 400°F.	1170	620	59	570	610
				6	" @ 480°F.	350	50	70	---	---
2372-1(A)BK-2600 (B) (C) (D)		510,000	GS1993	1	" @ 300°F.	171	887	28	41	83
				24	" @ 300°F.	465	825	38	100	176
				16	" @ 400°F.	430	513	50	177	342
				16	" @ 430°F.	229	37	75	---	---
Average Values	11317-5	430,000	GS1993	24	" @ 300°F.	390	810	44	110	200
				16	" @ 400°F.	390	520	50	210	280
				24	" @ 400°F.	390	200	61	---	---
				6	" @ 480°F.	380	90	69	---	---

Footnotes

- (1) Gen. Elec. SD-76 gum used, various batches as indicated
 (2) Press cure 15 minutes at 230°F.; oven cure as indicated

to the difference in average molecular weights and led to evaluation of GS199S Silica curing from this standpoint.

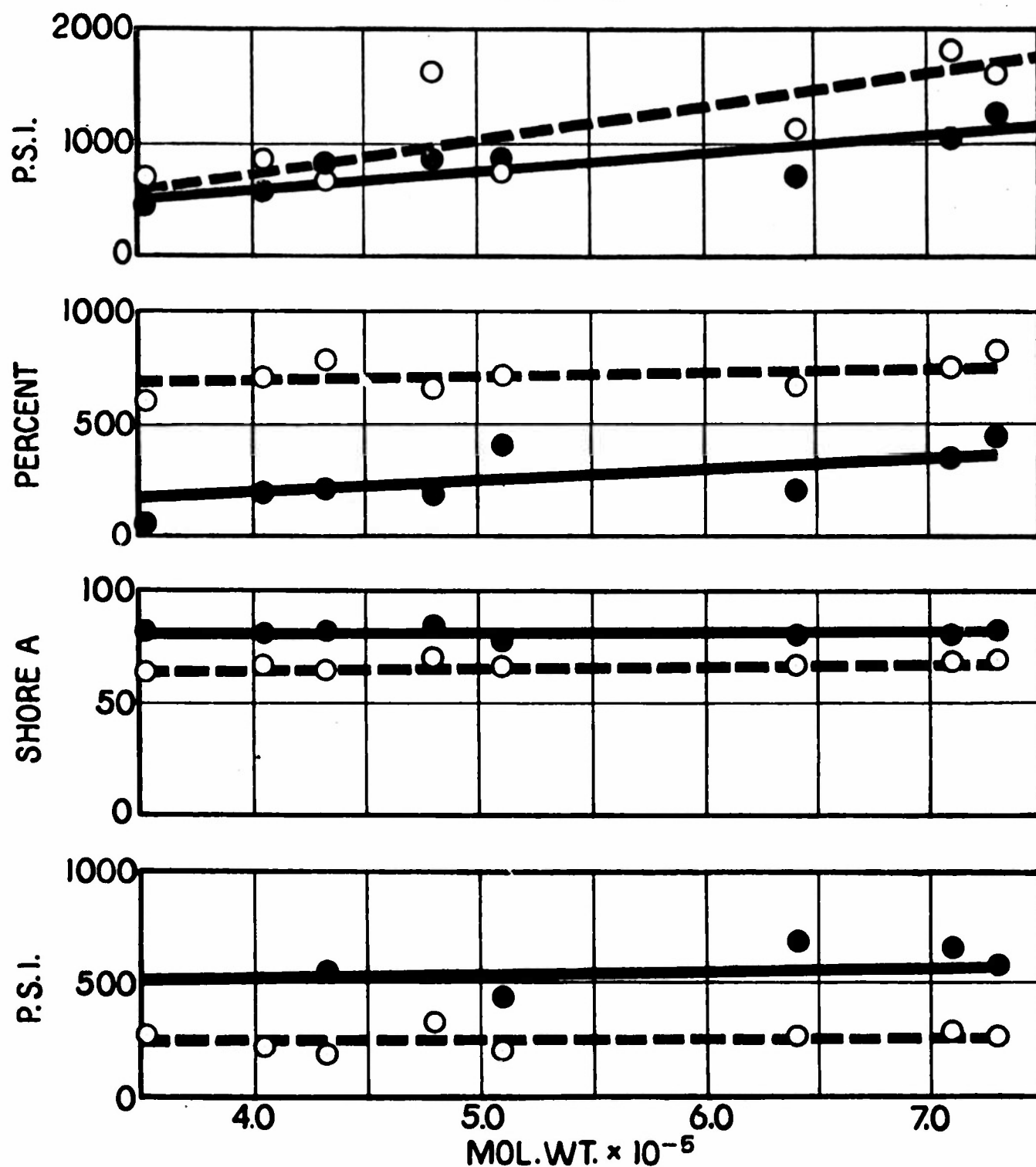
Table XXVII gives data on a batch of the 11317 gum which was separated by solvent precipitation into three different molecular weight fractions, which averaged 350,000, 410,000 and 640,000. Cures of the fractions show the highest tensile strength in the case of the highest molecular weight fraction, and little effect on other physical properties except that the highest fraction was also more stable at the 400°F. curing temperature.

Tables XXVIII and XXIX contain data for a series of cures with 15 and 25 volumes of GS Silica in five different batches of SM-76. These batches were used, as received, and their average molecular weights were determined by the viscosity method as previously described (page 71). Average molecular weights ranged from 430,000 for Batch No. 11317 to 730,000 for Batch No. B-5946.

With 15 volumes of GS Silica (Table XXIX), the best reinforcement occurred with Batch No. B-5946 of 730,000 molecular weight.

All of the available batches of SM-76 were compounded with 25 volumes of GS199S silica, the data being given in Table XXVIII and presented graphically in Figure II. There are several interesting points evident from inspection of the data and graph. There is a definite increase in tensile strength as molecular weight increases,

FIG. XI



GS SILICA IN SE-76 OF VARYING MOLECULAR WT.
25 VOLS. NO B.P.

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA 44-109-qm-64

○ — CURED @ 300°F.
● — CURED @ 400°F.

i.e., from 200-300 p.s.i. at 430,000 molecular weight to 1000-1750 p.s.i. at 700,000 molecular weight. This occurs with either a 300° or 400°F. cure, although the result is more easily detected at the lower temperature of cure. This accounts for the failure to produce high-tensile-strength GS199S Silica stocks with the regularly available, low-molecular-weight variety of SE-76. Figure XI shows that as gum molecular weight increases, the tensile strength plot indicates the biggest increase, with a slight effect observable in elongation improvement. Other properties are not changed appreciably.

These data show that SE-76 rubber, to be most effective in compounding with GS Silica, should be of about 700,000 average molecular weight, or more. This grade of polymer shows better tensile strength than the presently favored, lower viscosity type currently sold by the General Electric Company. It is recognized that softer, lower molecular weight gum is easier to mill and easier to "freshen" by milling after having been mixed and aged.

DuPont GS199S Silica as a Reinforcing Agent

DuPont GS199S Hydrophobic Silica was brought to our attention late in 1951. The properties of this material are given in Table XII and in more detail below. It had already been extensively evaluated by DuPont as an inorganic thickening agent for oils to make lubricating greases.

The structure of the pigment has not yet been revealed. The product information sheet put out by Grasselli Chemicals Department, E.I. du Pont de Nemours & Company, Inc. stated that GS199S Silica has the following properties:

1. Extremely small ultimate particle size
2. High specific surface area
3. Pronounced hydrophobic and organophilic properties
4. Ease of dispersion in organic systems with conventional milling procedures
5. Low bulk density

Other obvious characteristics may be listed:

6. An organic constituent to the extent of approximately 15 percent which is removable by heating in air at 480°F.

7. A pronounced capacity for taking up static charges

Other properties disclosed by DuPont include the following:

- | | |
|--|----------------------------|
| 1. Surface area by nitrogen absorption | 250-300 m ² /g. |
| 2. Bulk density | 7 lb./cu ft.,
average |
| 3. SiO ₂ | 84-88% |
| 4. pH in 50-50 methanol-water mixture | 7.5-9.5 |
| 5. Physical form of silica | Amorphous |

It was also revealed that the pigment is chemically stable at ordinary temperatures except in the presence of alkalies and hydrogen fluoride. It is subject to attack by oxygen above 200°F., with loss of its hydrophobic

Plate 8



Mag. x 72,600

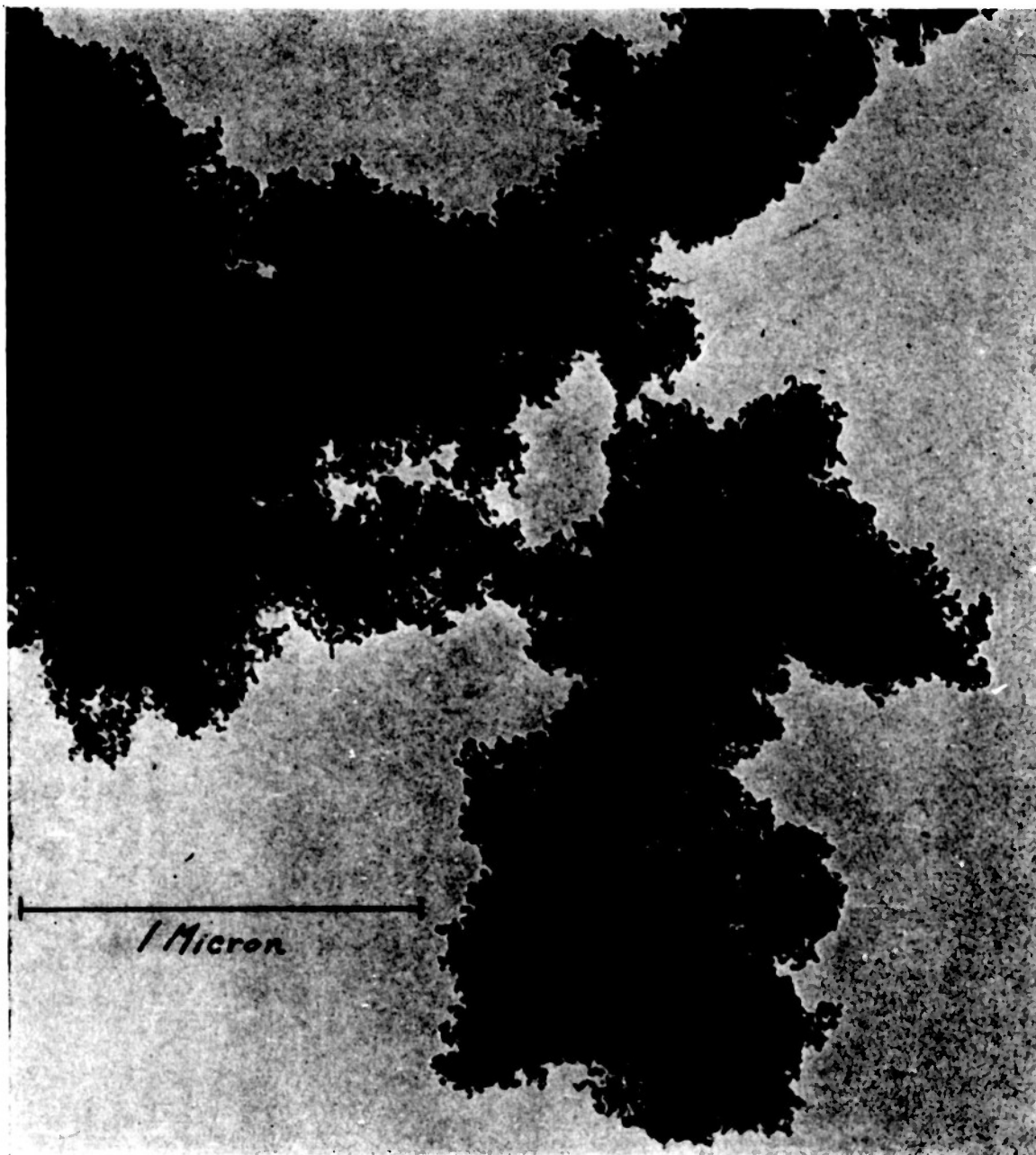
Sample No. E-1
Negative No. 2997D
Magnification: 6600
Enlarged: 11.0

Date: 11/29/51
Paper: F-2
Stop: 11
Exposure: 20 sec.

Remarks: GS199S Pigment on Collodion (Spark dispersed)

Smallest particles 0.006-0.014 μ

Agglomerates 1.0 x 2.0 μ



ELECTRON MICROGRAPH OF GS-199S PIGMENT

72,600 X

PLATE 8

TABLE XXX

CS1993 SILICA WITH VARIOUS BENZOYL PEROXIDE AND CURES¹

Compd. No.	Benzoyl Peroxide Vol. Wt. (%)	Pigment	Oven Cure	Physical Properties ²				Comp. Set (%) ³
				Stress @ 200%	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	
2050-1	1.0	15	24 hrs. @ 300°F. 24 hrs. @ 400°F.	374 630	840 710	475 275	63 70	85.5 44.9
2050-2	1.5	15	24 hrs. @ 300°F. 24 hrs. @ 400°F.	487 720	960 870	400 275	65 73	83.0 52.5
1967-2	2.0	15	24 hrs. @ 300°F. 24 hrs. @ 400°F.	597 795	975 795	350 200	60 76	83.1 61.5
1996	1.0	25	1 hr. @ 300°F. 24 hrs. @ 300°F. 24 hrs. @ 400°F.	276 554 ---	1930 1660 795	850 550 63	73 83 93	96.7 86.5 42.1
1996-1	1.5	25	1 hr. @ 300°F. 24 hrs. @ 300°F. 24 hrs. @ 400°F.	308 610 ---	1680 1325 795	700 463 75	75 85 94	93.5 83.5 43.3
1985	2.0	25	1 hr. @ 300°F. 24 hrs. @ 300°F. 24 hrs. @ 400°F.	419 684 ---	1615 1170 795	613 388 75	77 85 93	94.5 84.8 49.0

¹Compounded with G.E. 81176 silicone gum; indicated concentration of peroxide²Press cure 15 min. @ 250°F. Oven cures as indicated³Compression set according to A.S.T.M. D-395-49T (Method B), 22 hrs. @ 300°F.

Plate 9

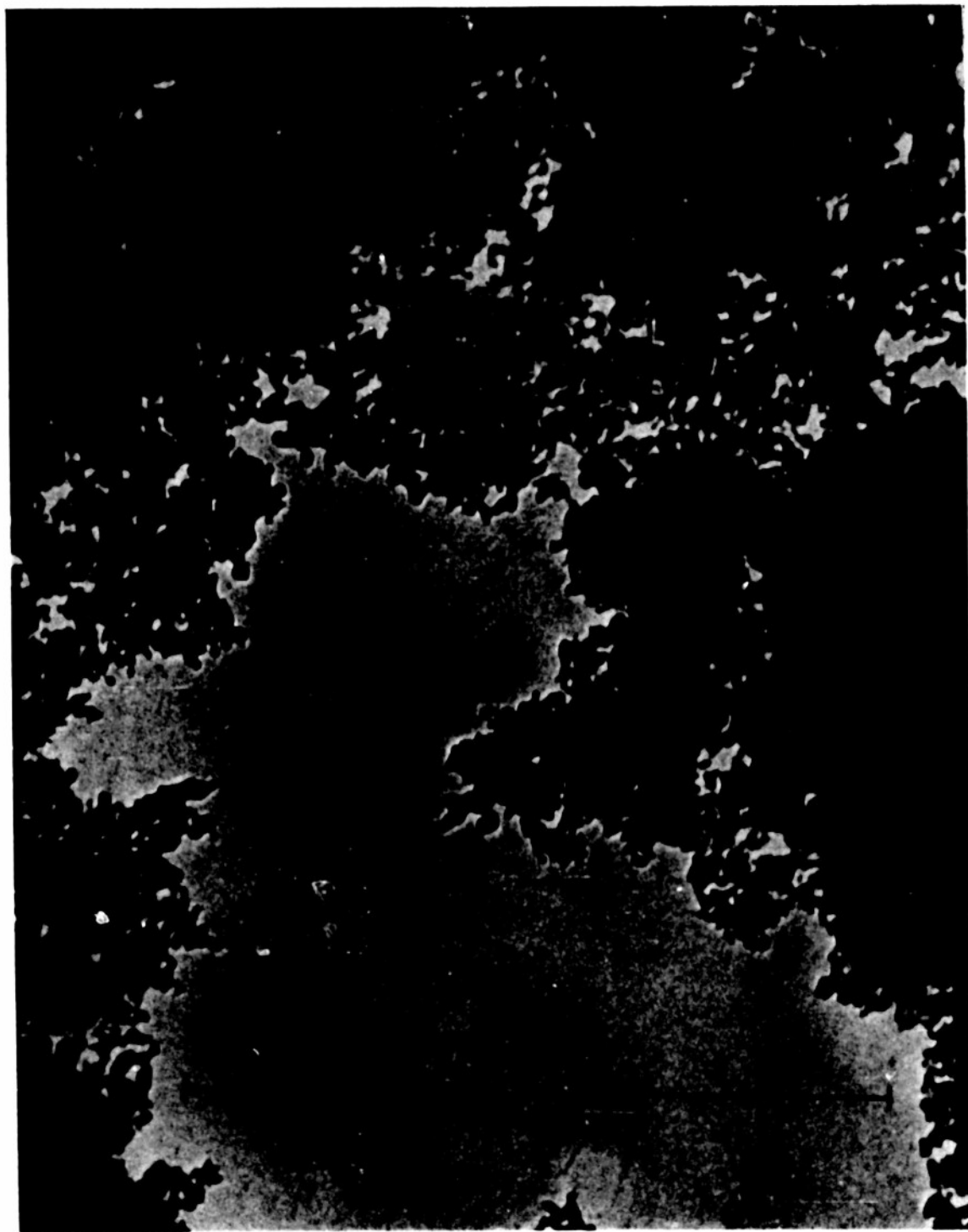
1 Micron

Mag. x 142,100

Sample No. E-5
Negative No. 3078C
Magnification: 20,300
Enlarged: 7.0

Date: 1/10/52
Paper: F-3
Stop: 11
Exposure: 30 sec.

Remarks: Santocel C on collodion (Spark dispersed, Pd.
Shadow)
Small particles 0.005-0.015 μ . Shows Aerogel
structure 0.01-0.10 μ pores.



LECTRON MICROGRAPH OF SANTOCEL-C PIGMENT

142,000 X

PLATE 9

Plate 10


1 Micron

Mag. x 46,200

Sample No. E-6
Negative No. 3141C
Enlarged: 7.0
Magnification: 6600

Date: 2/1/52
Paper: F-2
Stop: 8
Exposure: 20 sec.

Remarks: GS1998 in SE-76 (15 vol. cure 1 hr. @ 300°F.)
Section, Methacrylate Removed, Pd. Shadow.



ELECTRON MICROGRAPH OF GS-199S PIGMENT IN SE-76

46,200 X

PLATE 10

properties.

It was also claimed that GS199S Silica has a strong reinforcing effect in natural rubber and in standard GR-S, Cold GR-S and Neoprene GN.

Particle diameter of the ultimate particle of GS199S Silica is approximately 0.01 microns. This is not greatly different from that of Santocel C. One of the first features of GS199S Silica was that it could be incorporated in silicone rubber to the extent of 50 volumes per hundred of rubber. Such high loadings would not be very practical but may be compared with Santocel C, for example, with which 27.5 volumes is the maximum loading, even though the ultimate particle sizes are practically identical.

It must be assumed that the organic coating on GS199S Silica temporarily prevents penetration of the liquid silicone rubber into pores of the filler. This occurs fairly rapidly in the case of Santocel C. In both cases, a structure is formed as the liquid silicone rubber is absorbed by the porous silica filler, but development of this structure is retarded in the case of GS199S, so larger volume loadings can be incorporated. Repeated milling breaks down the structure effect and tends to restore plasticity. It is our feeling at this time that a 25-volume loading is probably the maximum that is likely to be used commercially with GS199S, as compared with approximately 16 volumes, ordinarily considered the maximum with Santocel C.

The table on the opposite page shows the magnitude of the physical properties that can be obtained with GS199S Silica in SE-76 rubber. These tests were obtained in the presence of variable benzoyl peroxide. They show that the concentration of benzoyl peroxide has little effect on the hardness or modulus, especially after 24 hours at 400°F. Benzoyl peroxide has a slightly adverse effect on compression set. Full cures at 400°F. appear to be impractical with 25 volumes of GS199S - the compounds stiffen and harden too much.

The table shows the highest tensile strengths that we had ever seen with silicone rubber at the time that they were measured. Unfortunately, high tensile strength, heat resistance and compression set resistance do not seem to be obtainable in one and the same slab.

It seemed obvious that the benzoyl peroxide used in the recipes in Table XXX was doing no good whatsoever. When it was removed, it was found that curing occurred in its absence. In the absence of benzoyl peroxide, optimum tensile strength is not reached in a one-hour oven cure at 300°F., as occurs when it is present. The maximum tensile strength is reached in about 16 to 24 hours at 300°F., or in 2 to 6 hours at 400°F. Curing at 400° or 480°F. hardens and stiffens the GS199S recipes at a much faster rate than it does recipes not containing GS199S,

but the benzoyl peroxide plays no important role.

The following pages of this report are devoted to GS199S compounding and the effect of varying concentration, time and temperature of cure, molecular weight of the rubber, methods of mixing, etc.

Electron micrographs of GS199S resemble those taken of Santocel C. The ultimate particles are of approximately the same size, 0.01 microns, but the aggregates of Santocel C are slightly larger. The similarity of the two pigments stops here, for Santocel C is definitely hydrophilic while GS199S is hydrophobic.

Electron micrographs of GS199S, Santocel C and GS199S in SE-76 rubber, face this page. These show the particulate structure of the fillers, the large porous aggregates and the way the rubber penetrates and surrounds the GS199S in a 15-volume recipe.

The organic coating in GS199S was shown to be essentially butyl alcohol. It can be removed, intact, by dissolving the silica substrate in 3N sodium hydroxide. This was done, and positive identification of at least one half of the coating was made. It was found to be normal butyl alcohol. The coating is oxidizable upon heating in air but is not removed by heating at 480°F. in vacuo (4 percent weight loss under these conditions). It appears that the coating is chemically bonded to the silica.

It may be surmised that partial removal of the

chemically bonded coating during oven curing of silicone GS199S mixtures is connected in some way with the development of vulcanization bonds. The mechanism by which this vulcanization may occur has not been worked out.

In Report No. 12, the results of over a hundred tests in which GS199S was used as the curing agent, were reported. These could be divided into two main groups, those in which high molecular weight rubber for Batch No. 5946 was used and those in which softer, lower molecular weight rubber for Batch No. 11317 was used. The effect of the molecular weight of the rubber has been discussed previously.

From the tables in Report No. 12, we find that the vulcanizing action is too dilute when less than 10 volumes of GS199S Silica is present and too concentrated when more than 30 volumes is present. Maximum tensile strength appears to be obtained at 20 to 25 volume loading. Since the filler is also serving as curing agent, it is difficult to decide whether to avoid overcuring by using 10 to 15 volumes of GS199S or to achieve maximum reinforcement by using 20 to 25 volumes.

It will be shown later that the overcuring tendency is not strong at 300°F. Tests carried out with a relatively short cure at 300°F. are best, therefore, for an examination of the effect of the volume loading of GS199S Silica. The tests shown in the table below were obtained with a

24-hour cure at 300°F. These vulcanizates may be considered fully cured, as optimum tensile strengths are generally reached in this period.

TABLE XXXI

EFFECT OF VOLUME LOADING OF GS199S IN SR-76*
NO BENZOYL PEROXIDE - 24 HRS. AT 300°F.

<u>Vol.Per</u> <u>100 of SR-76</u>	<u>Stress@</u> <u>200%</u>	<u>Stress@</u> <u>400%</u>	<u>Tensile</u> <u>p.s.i.</u>	<u>Elong.</u> <u>%</u>	<u>Hardness</u> <u>Shore A</u>
5	28	30	32	463	11
10	81	148	547	925	26
15(AV. 2 tests)	180	310	1550	930	47
25(AV. 4 tests)	252	450	1640	845	67

*Batch B-5946

The high tensile strength of GS199S vulcanizates such as those in the table above are the product of moderate stiffness and high elongation. To this extent, GS199S resembles Alon which imparts similar stress-strain properties. The stress-strain curve of GS199S compounds is peculiar in that there is a hump near the origin, characterized by high initial stress at low elongations. This "structure" irregularity is removed when test strips are stressed once or twice before being tested to break. Ultimate tensile strength and elongation are not changed much by such treatment, although the stress-strain curve is lowered generally at low extensions. No explanation of this irregularity can be offered at this time.

Higher volume loadings of GS199S lead to the formation

of plasticlike slabs. These tend to be brittle, if cured at high temperatures. The maximum volume loading that was reached on the laboratory mill was 52.5 volumes per hundred of rubber.

High-Temperature Properties with GS199S Silica

Due to the persistent curing action of GS199S Silica, loss of tensile strength and elongation, common in all oven curing of silicone stocks, is much greater when these contain GS199S silica than when they do not. When curing or aging is limited to 300°F., GS199S recipes are fairly stable. At the time that this contract was closed, we were unable to prevent rapid decay of tensile strength and, especially, elongation during high-temperature aging or curing. Since the curing potential has been built into the pigment by its manufacturers who have combined therewith an organic coating removable not by heat alone but by oxidation plus heat, it seems probable that the curing action may, with further study, be controlled. When this is done, strong, resilient silicone rubber will result from the use of low percentages of the pigment, and very tough, tightly cured, highly reinforced compounds will result when high loadings are used. Data in the following sections of this report will show the degree of overcuring commonly obtained with GS199S.

TABLE XXII

OVEN CURING GS SILICA COMPOUNDS

Compound No.	Pigment	Vol. % Benzoyl Pig.	Wt. % Peroxide	(A)	(B)	(C)	(D)	(E)	(F)	(G)	1 hr. @ 300°F.	Comp Set (3)	Tensile Strength p.s.i.	Elongation Percent	Hardness Shore A	Stress @ 200'	Stress @ 400'
2344	GS Silica	25	0	(A)	(B)	(C)	(D)	(E)	(F)	(G)	1 hr. @ 300°F.	107	212	875	44	75	100
				(B)	(C)	(D)	(E)	(F)	(G)		"	103	413	862	47	108	150
				(C)	(D)	(E)	(F)	(G)			"	101	550	813	51	134	205
				(D)	(E)	(F)	(G)				"	97	638	813	53	153	235
				(E)	(F)	(G)					"	93	875	768	55	200	---
				(F)	(G)						"	---	812	700	58	356	---
				(G)							"	---	932	537	63	475	---
2344-1	GS Silica	25	0	(A)	(B)	(C)	(D)	(E)			1 hr. @ 400°F.	99	398	762	46	115	---
				(B)	(C)	(D)	(E)				"	96	854	636	52	240	---
				(C)	(D)	(E)					"	72	643	250	77	570	---
				(D)	(E)						"	64	600	100	81	---	---
				(E)							"	53	626	37	85	---	---
2344-2	GS Silica	25	0	(A)	(B)	(C)	(D)	(E)			1 hr. @ 450°F.	95	665	513	60	282	522
				(B)	(C)	(D)	(E)				"	49	---	---	---	---	---
				(C)	(D)	(E)					"	52	525	25	82	---	---
				(D)	(E)						"	56	523	50	84	---	---
				(E)							"	76	581	25	35	---	---
2344-3	GS Silica	25	0	(A)	(B)	(C)	(D)	(E)			1 hr. @ 480°F.	---	491	125	74	---	---
				(B)	(C)	(D)	(E)				"	---	445	25	85	---	---
				(C)	(D)	(E)					"	---	Brittle	---	90	---	---
				(D)	(E)						"	---	"	---	90	---	---
				(E)							"	---	"	---	90	---	---

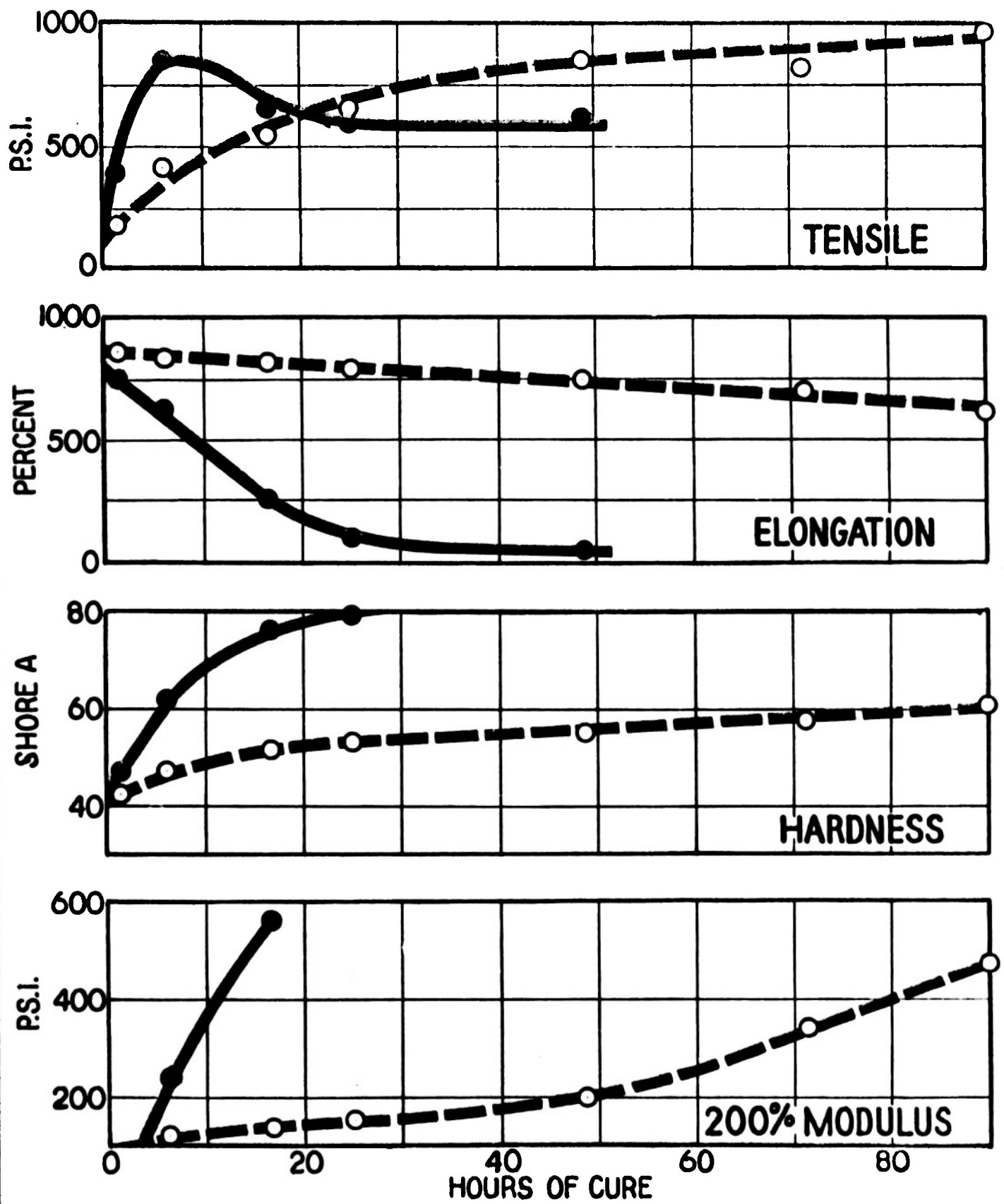
Footnotes:

(1) Gen. Elec. SE-76 silicone gum (Batch No. 11317) used.

(2) Press cure 15 minutes at 230°F.; oven cure as indicated.

(3) Percent of original deflection. By A.S.T.M. D-395-49T (70 hours at 300°F.).

FIG. XII



OVEN CURES OF GS SILICA STOCK
25VOLS. NO B.P.

CONNECTICUT HARD RUBBER COMPANY
U.S. GOVT. CONTRACT DA 44-109-qm-64

○ — CURED AT 300°F
● — CURED AT 400°F

Rate of Cure of GS199S Silica Mixes

Tensile strength and elongation data were obtained at 300°F., 400°F., 450°F. and 480°F. at various times of cure on a 25-volume mix with GS199S Silica in standard SE-76 (about 430,000 molecular weight). Equivalent cures were reached at approximately 50 hours at 300°F. and 6 hours at 400°F. At 450° and 480°F., the equivalent time would have been less than one hour but cures shorter than one hour were not attempted. The data are not accurate enough for a determination of the temperature coefficient.

The rubber used here was the low-molecular-weight gum, Batch 11317. Tensile strengths of 800 to 1000 p.s.i. were reached only by curing for 48 to 96 hours at 300°F. or for 6 hours at 400°F. The low-molecular-weight rubber does not provide sufficient stiffness to result in high tensile strength. At 300°F., there was very little tendency toward overcuring. One might conclude that at 300°F. the cured product is reasonably stable, although it is obviously still undergoing curing. However, at 400°, 450° or 480°F., there is no question that the 25-volume loading of GS199S is rapidly overcuring the product. The rates of cure at 300° and 400°F. are easily analyzed by looking at Figure XII.

As in benzoyl peroxide-cured silicone rubber, the compression set does not begin to fall to a satisfactory

TABLE IVIII

HIGH-TEMPERATURE CURING OF GS SILICA STOCKS

Compound No.	Pigment	Volume % Pigment	Oven Cure	T	E	n	Stress @ 200%
2261 (A)	GS Silica	10	1 hr. 480°F.	199	350	35	143
(B)			4 " "	153	163	45	---
(C)			8 " "	176	138	43	---
(D)			8 " "	170	163	43	---
(E)			16 " "	131	113	43	---
2262 (A)	GS Silica	15	1 hr. 480°F.	400	300	57	364
(B)			4 " "	351	100	69	---
(C)			8 " "	339	83	71	---
(D)			8 " "	344	75	70	---
(E)			16 " "	291	50	72	---

(1) General Electric 53-76 silicone gum used; no curing agent.

(2) Press cure 15 min. @ 230°F.; oven cures as indicated.

level until the elongation has dropped far down. It is interesting to observe that overcuring to a degree leading to embrittlement definitely does not occur at 300°F. (up to 96 hours) but occurs quickly as the oven temperature is raised. The data may be found in Table XXXIII and Figure XII.

In Table XXXIII, the rate of cure of 10 and 15 volume mixes at 480°F. can be followed. Using elongation as an index of cure for want of a better one in this case, we see that a 10-volume mix required about 20 hours at 480°F., a 15-volume mix required 4 hours, and a 25-volume mix (Table XXXII) required about 2 hours to drop to 100 percent elongation. Thus at lower concentrations of GS1993 Silica, the overcuring tendency is diminished; unfortunately such mixings are not adequately reinforced. Mixtures of GS1993 Silica with reinforcing pigments have been tried with mixed success, and further work is indicated here.

Curing with Benzoyl Peroxide

It might be expected that cross-linking of silicone rubber reinforced by GS1993 Silica with benzoyl peroxide might stabilize the system with respect to 480°F. curing. Therefore a study of press and oven curing with various proportions of benzoyl peroxide was carried out in an attempt to overcome high-temperature brittleness.

TABLE XXIV

PRESS CURING GS SILICA COMPOUNDS

Com- pound No.	Pigment	Vol. % Benzoyl Pig. Peroxide	Ut. %	Press Cure	Oven Cure	Tensile Strength P.s.i.	Elongation Percent	Hard- ness Shore A	Stress Stress C 200% 400%
2378	GS Silica	25	2.0	(A) 10 min. @ 210°F.	1 hr. @ 300°F. 3 hrs. @ 480°F.	1020 Brittle	500	74 89	364 715
				(B) 10 min. @ 230°F.	1 hr. @ 300°F. 3 hrs. @ 480°F.	1300 Brittle	688	73 91	313 613
				(C) 10 min. @ 250°F.	1 hr. @ 300°F. 3 hrs. @ 480°F.	1320 Brittle	713	73 90	321 580
2378-1	GS Silica	25	0.5	(A) 10 min. @ 210°F.	1 hr. @ 300°F. 3 hrs. @ 480°F.	795 Brittle	800	60 93	175 260
				(B) 10 min. @ 230°F.	1 hr. @ 300°F. 3 hrs. @ 480°F.	510 Brittle	825	60 86	130 200
				(C) 10 min. @ 250°F.	1 hr. @ 300°F. 3 hrs. @ 480°F.	520 Brittle	888	60 88	130 180

Footnotes:

- (1) Gen. Elec. SE-76 gum used
(2) Press and oven cures as indicated

1. Press Curing Data

Variation of press curing temperature was carried out with 25-volume GS199S Silica stocks containing 0.5 and 2.0 percent benzoyl peroxide. Low-molecular-weight gum, Batch 11317, was used. Data are given in Table XXIV. With 0.5 percent peroxide, reinforcement was lowered as the press curing temperature was raised. The same was true using 2 percent peroxide, as indicated by the modulus data. These data are comparable to those in Tables XVI and XVII, and again suggest that peroxide decomposition products are operative in depolymerizing the GS-76 at the higher press temperatures. None of these variations served to keep the 480°F. cured slabs from becoming stiff and brittle and therefore unsatisfactory.

2. Oven Curing Data

Table XXV shows data on 400° and 480°F. oven cures of 15 and 25 volume GS Silica stocks with varying benzoyl peroxide. The regularly available lower molecular weight GS-76 siloxane polymer (Batch No. 11317) was used.

The purpose of this series of tests was to determine the high-temperature curing properties of the low-molecular-weight polymer with GS199S Silica plus peroxide. Fifteen-volume stocks withstand 44 hours at 400°F. without becoming brittle. However, from the standpoint of tensile strength, the 12-hour cures at 400°F. were superior.

With 25 volumes of GS Silica, the 12-hour cure at

TABLE XXV
OVEN CURING VARIOUS GS SILICA COMPOUNDS

Compound No.	Pigment	Vol. % Benzoyl Peroxide	Wt. %	Oven Cure	Tensile strength p.s.i.	Elongation Percent	Hardness Shore A	Stress 200%	Stress @ 400%
2265-1	GS Silica	15	0	12 hrs. @ 400°F. 44 hrs. @ 400°F. 16 hrs. @ 480°F.	276 362 346	518 225 50	44 64 70	155 353 ---	226 --- ---
2265-2	GS Silica	15	0.5	12 hrs. @ 400°F. 44 hrs. @ 400°F. 16 hrs. @ 480°F.	567 494 325	525 200 75	55 67 67	287 430 ---	455 --- ---
2265-3	GS Silica	15	1.0	12 hrs. @ 400°F. 44 hrs. @ 400°F. 16 hrs. @ 480°F.	678 425 314	475 163 63	63 71 68	353 404 ---	592 --- ---
2266-1	GS Silica	25	0	12 hrs. @ 400°F. 44 hrs. @ 400°F. 16 hrs. @ 480°F.	319 494 39	650 50 10	72 85 93	314 --- ---	478 --- ---
2266-2	GS Silica	25	0.5	12 hrs. @ 400°F. 44 hrs. @ 400°F. 16 hrs. @ 480°F.	897 516 149	525 50 10	81 83 92	477 --- ---	772 --- ---
2266-3	GS Silica	25	1.0	12 hrs. @ 400°F. 44 hrs. @ 400°F. 16 hrs. @ 480°F.	915 530 234	412 25 25	62 88 94	552 --- ---	868 --- ---

Footnotes:

- (1) Gen. Elec. SE-76 silicone gum used (Batch No. 11317)
- (2) Press cure 15 minutes at 230°F.; oven cure as indicated

400°F. is the only satisfactory one, and all properties suffer with further curing. Other data show that with benzoyl peroxide present, the highest elongation and tensile strength are obtained in short cures, 1 hour at 300° or 400° F., these properties falling off fairly rapidly with further curing. This is attributable to the effect of the pigment, the ultimate properties being independent of the concentration of benzoyl peroxide.

Effect of Milling GS199S Mixes

Fine powders are difficult to disperse in silicone rubber; the finer they are the greater the difficulty. The difficulties in the case of silicone rubber are not the same as those encountered in ordinary rubber compounding. There, if one proceeds slowly to add the fine powder, the only thing that happens is that the batch becomes very hot and very tough as high loadings are reached. With silicone rubbers, the first sign of difficulty is noted when the batch loosens from the rolls and falls into the pan. The lack of cohesiveness of silicone rubber to itself, or adhesiveness to steel-mill rolls makes mill-mixing difficult. Fast mills, tight rolls and careful adjustment of batch-size to fit the mill are essential. GS199S Silica makes no exception to the rule. Our observations are that GS199S is somewhat more difficult to handle than Alon or Santocel C on the laboratory mill.

TABLE CCXVI

EVALUATING SHELF-AGING TESTS OF 25-VOLUME GS199S MASTER BATCH

Compound No.	Date of Remilling	Stress @ 200%	Stress @ 400%	Tensile Strength p.s.i.	Elongation percent	Hardness Shore A
1985-A (B1) (control)	4-9-52	179	274	1695	900	56
1985-A (B2)	4-14-52	170	234	1570	925	55
1985-A (B3)	4-17-52	160	254	1385	900	55
1985-A (B4)	4-21-52	171	282	1635	950	54
1985-A (B5)	4-23-52	190	288	1615	900	53
1985-A (B6)	4-25-52	189	295	1417	368	50
1985-A (B7)	4-28-52	184	296	1563	900	53
1985-A (B8)	4-30-52	178	288	1310	875	52
1985-A (A1) Not remilled(aged 2 months)		217	371	1768	800	64

The stocks were compounded with S3-76 silicone gum(Batch #5946).

No benzoyl peroxide was used as a curing agent.

The press cure was 15 minutes at 230°F.

The master batch was heated continuously at 125°F. until date of remilling, except 1985-A(A1) which was aged 2 months at room temperature. Oven cure was 1 hour at 400°F.

Production-scale batches have not been attempted.

It is found that standard (433,000) molecular weight rubber is far more easily compounded with GS199S than tougher grades of rubber. The latter may easily require twice as long to mix in the laboratory. Higher physical properties result, as shown on page 75. The plasticizing action of lower molecular weight polymer is offset, with GS199S, by the lower properties that result.

When a given batch is mixed, good practice recommends aging and remilling after a day or two. Apparently a structure is built up, as is the case with Santocel C, and remilling seems to restore tack, pliability and plastic flow properties. Table XLVI shows the effect of prolonged storage of a master batch of 25 volumes of GS199S in SE-76.

A large master batch was prepared, containing 25 volumes of GS199S Silica. It was then exposed at 125°F. for 21 days, with samples being removed periodically. The samples were remilled to establish whether the stock appeared to be setting up in storage, and then were cured and tested. No change in workability on the mill could be detected. The results are shown in Table XXXVI. There appears to be no consistent change in the properties of this 25-volume stock in 21 days at 125°F.

The same master batch, aged for two months at room temperature (April and May), was then cured and tested without remilling. Except for a slight stiffening, which

TABLE XXXVII

REMILLING GS SILICA STOCKS

Compound No.	Pigment	Treatment	Volume % Pigment	Oven Cure	T	E	H	Stress @ 200%	Stress @ 400%
2284	GS Silica	Control Remilled (3)	15 "	{ 24 hrs. 400°F. 9 hrs. 480°F.	380 440	117 400	58 55	--- 254	--- 440
2285	"	Control Remilled (3)	25 "	{ 24 hrs. 400°F. 9 hrs. 480°F.	583 798	88 375	83 75	--- 508	--- ---
2286	"	Control Remilled (3)	30 "	{ 24 hrs. 400°F. 9 hrs. 480°F.	150 734	0 150	93 89	--- ---	--- ---
2287	"	Control Remilled (3)	35 "	{ 24 hrs. 400°F. 9 hrs. 480°F.	135 731	0 63	95 93	--- ---	--- ---

(1) General Electric SE-76 silicone gum used; no curing agent

(2) Press cure 15 min. @ 230°F.; oven cure as indicated

(3) Compounds were remilled each day for 3 days before curing.

could have been reduced by remilling, the results were satisfactory.

Banbury-mixed batches of GS1996 in SE-76 were prepared by the Grasselli Chemicals Department of DuPont. One such batch had evidently heated up to the point where it had scorched, but another was successfully mixed and was usable.

Three separate remilling treatments were given to 15, 25, 30 and 35 volume mixings in standard SE-76. The data shown in Table IICVII include only cures of 24 hours at 400°F. plus 9 hrs. at 480°F. and reveal that a considerable improvement in elongation and therefore in tensile strength resulted from the additional milling. These are the best 480°F. cures that we have made. This amount of remilling might not be practical, but there seems to be a way here to counteract the overcuring tendency to some extent.

Plasticizers of GS1996 Mixes

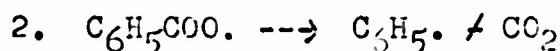
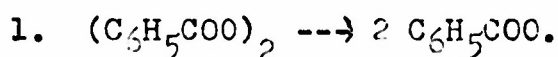
Many attempts were made to plasticize GS1996 compound to aid in withstanding high-temperature curing. Without exception, these attempts were failures. The details of these tests may be found in Report No. 13.

Rate of Decomposition of Benzoyl Peroxide and Mechanism of Vulcanization

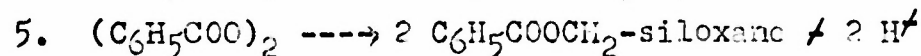
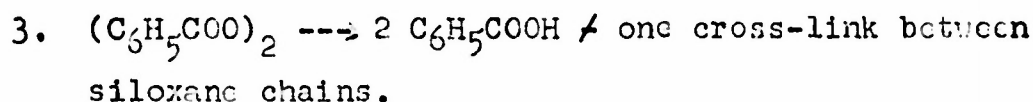
In Report No. 10, preliminary data were given on the

rate of decomposition of benzoyl peroxide in normal heptane as a solvent. This work was followed up, and Report No. 13 contained an account of the rate of decomposition of benzoyl peroxide in the presence of silicone rubber itself, as well as some experiments on the rate of vulcanization of liquid silicone, hexamethyldisiloxane, when reacted with p-chlorobenzoyl peroxide. All of this work is made the subject of a special section of this report which follows.

Acyl peroxides decompose under the influence of heat into free radicals which are able to react with suitably activated compounds. Thus benzoyl peroxide decomposes according to the following scheme:



The free radicals so formed may react with a silicone rubber as follows:



The study of the mechanism of vulcanization performed by this laboratory is divided into three parts.

1. Investigation of Reactions of Benzoyl Peroxide with Silicone Gum Dissolved in an Inert Solvent

This work showed the possibility of following the

reaction of benzoyl peroxide with a silicone polymer dissolved in an inert solvent. The most significant result obtained was that benzoic acid appeared in all cases as a product of the decomposition of benzoyl peroxide in the presence of heat and silicone polymer (Reaction 3), in amounts approximating 20 percent of the stoichiometric content. Carbon dioxide and benzene (Reaction 2) were also isolated, indicating a complex mode of decomposition of benzoyl peroxide through a free radical mechanism involving benzoate and phenyl fragments. It was also found that the neutralization of the benzoic acid, as formed, increased the efficiency of the benzoyl peroxide and effectively increased the extent of the vulcanization of silicone polymer.

2. Mechanism of Peroxide Vulcanization of Hexamethyldisiloxane

p-chlorobenzoyl peroxide was the curing agent used to study the vulcanization of hexamethyldisiloxane. The chloro-substituted peroxide was chosen because it allowed determination of the quantitative distribution of the various peroxide fragments by tracing the chlorine tagged groups. Hexamethyldisiloxane was chosen as the simplest prototype of silicone rubber polymers ordinarily used in industry. Free p-chlorobenzoic acid (Reaction 3) and carbon dioxide (Reaction 4) were isolated directly from the reaction mixture. p-chlorobenzoate groups attached to the

siloxane chain (Reaction 5) were cleaved by means of hydrolysis with strong alkali and recovered as p-chlorobenzoic acid. p-chlorophenyl groups also attached to the siloxane chain (Reaction 4) were identified from calculations based on the amount of carbon dioxide evolved through decarboxylation of p-chlorobenzoate groups.

TABLE XXXVIII
DISTRIBUTION OF CHLORINE IN PARTIALLY VULCANIZED
HEXAMETHYLDISILOXANE

	Weight in grams.	Percent based on total ini- tial chlo- rine.....	Percent based on total chlo- rine accoun- ted for.....
Chlorine present in orig- inal peroxide.....	1.269.....	100.00	
Chlorine present in free isolated p-ClBA.....	0.2796.....	22.03.....	27.9
Chlorine found in reac- tion mixture after removal of free p-ClBA.....	0.7620.....	60.04	
Chlorine corresponding to total CO ₂ evolved in original reaction.....	0.499.....	39.32.....	49.8
Chlorine present in chloro- benzoate groups hydro- lyzed in second re- action.....	0.224.....	17.65.....	22.3
Chlorine present in sub- stituents, total.....	0.723.....	56.97	
Chlorine unaccounted for, total.....	0.2664.....	20.92	
			<u>100.0</u>

A sample of the reaction mixture after removal of free p-chlorobenzoic acid was fractionally distilled, and three significant fractions were analyzed for chlorine content and molecular weight.

TABLE XXIX
MOLECULAR WEIGHT OF PARTIALLY VULCANIZED
HEXAMETHYLDISILOXANE

Weight percent of polymeric product based on reaction mixture.....	15.92
Molecular weight of Fraction I.....	250
Chlorine in Fraction I, percent.....	0.43
Molar ratio of chlorine to Fraction I.....	0.036
Molecular weight of Fraction II.....	855
Chlorine in Fraction II, percent.....	4.47
Molar ratio of chlorine to Fraction II.....	1.08
Molecular weight of Fraction III.....	1060
Chlorine in Fraction III, percent.....	7.86
Molar ratio of chlorine to Fraction III.....	2.34

This work has shown that, in addition to benzoic acid which was known to be a product of the vulcanization of silicone rubber by benzoyl peroxide, a large amount of substitution into the siloxane molecule occurs. In fact, substitution consumes 70 to 80 percent of the peroxide accounted for, with 20 to 30 percent appearing as benzoic

acid. Some of the substituted groups are benzoate groups and thus are the source of carbon dioxide which escapes during the oven curing of rubber. When carbon dioxide escapes, benzoate groups become phenyl groups. Substitution and cross-linking occur simultaneously in the same molecule and are probably related, since more substitution occurred in the more highly cross-linked molecules.

3- Mechanism of Vulcanization of Silicone Rubber

This part of the study was performed to investigate the formation of benzoic acid in the silicone rubber during press cure. This was accomplished by compounding several slabs of General Electric SE-76 gum with Santocel C and varying percentages of benzoyl peroxide and giving them different press cures. The press-cured slabs were analyzed for benzoic acid formed, and residual benzoyl peroxide, before oven curing one hour at 300°F. Physical properties of the oven cured slabs were determined.

Results

Expectedly, the amount of benzoic acid formed was proportional to the amount of benzoyl peroxide initially present. At initial concentrations of 6 percent or less, only 4 to 10 percent of the benzoyl peroxide appeared as benzoic acid. This is much less than was found in experiments involving the reaction with silicone oils. With 8 percent of benzoyl peroxide added, 27 percent of it was transformed to benzoic acid.

<u>Percent B. P. Present</u>	<u>Percent B. A. Found*</u>	<u>Percent B. A. Found **</u>
2	.126	6.3
4	.242	6.05
6	.442	7.37
8	2.168	27.06

* percent based on 100 parts of rubber

** percent based on initial benzoyl peroxide

There was no proportional variation in the amount of benzoic acid found as time and temperature were varied from 5 minutes at 212°F. to 10 minutes at 300°F.

Peroxide decomposition was 85 percent complete at all

curing conditions more severe than a 10-minute rise to 250°F. plus 5 minutes at 250°F. Excellent cures were obtained, with only 44 percent decomposition of the peroxide, with a 10-minute rise to 250°F., followed by cooling to room temperature. Excellent cures were obtained with a 5-minute rise to 212°F. plus 10 minutes at 212°F., with only 41 percent decomposition of the peroxide. There seems to be no justification for carrying out press curing longer or at a higher temperature.

Swelling of Silicone Rubber, Molecular Weight between Cross-Links and the Cohesive Energy Density

In Report No. 10 and Report No. 11, a very thorough study of the structure of vulcanized silicone rubber, carried out by R. L. Hauser of this laboratory, was reported. This work was done by swelling samples of vulcanized silicone rubber and following carefully the rate and magnitude of the swelling. Flory has derived equations relating the molecular weight of the rubber with the volume fraction of polymer in the swollen network. There is one parameter (χ) in the equation which has a different value for each rubber and solvent pair. Values of χ are known for most rubber and solvent pairs, but were unknown for silicone rubber with the various solvents. By making ingenious approximations, Mr. Hauser was able to arrive at limiting values for both the molecular weight and the parameters themselves. The molecular weight referred to

above is that designated as M_c , defined as the molecular weight of polymer between cross-links. Its value therefore gives a measure of the degree of cross-linking or the degree of vulcanization.

This section of this report is devoted to a summary of Mr. Hauser's work on swelling. Included among other results is direct proof that the first two percent of benzoyl peroxide is far more efficient in its cross-linking action than the next six percent. Another theoretically important conclusion is that the cohesive energy density of vulcanized silicone rubber is $7.50 \pm .05$. Mr. Hauser also worked out the technique of carrying out swelling measurements over long periods of time. It was found that the swelling is affected by the simultaneous extraction of polymer by the swelling liquid.

It should be possible to continue this theoretical work on silicone rubber which is vulcanized by GS199S Silica, to establish the M_c value, i.e., the molecular weight between cross-links formed by the interaction of the GS199S pigment and the rubber.

It is known that most oils and fuels deteriorate rubber products, silicone rubber being affected to such an extent that its residual strength, when swollen, is practically zero.

The present study was carried out with the aim of shedding some light on the mechanism of swelling and the

TABLE XL

EQUILIBRIUM V_2 VALUES FOR SE-76 VULCANIZATE(V₂ is the volume fraction of polymer in the swollen network)

<u>Solvent</u>	<u>Solubility Parameter (cal./c.c.)¹</u>	<u>V₂</u>	<u>μ #</u>
Perfluoro(methyl- cyclohexane)	6.5	1.0	Neg.
N-Hexane	7.27	.138	.323
N-octane	7.55	.141	.308
Methylcyclohexane	7.83	.137	.333
Cyclohexane	8.20	.148	.400
D-Limonene	8.50	.183	.416
Xylene	8.82	.182	.458
Toluene	8.91	.170	.439**
Benzene	9.16	.206	.521
Methylethylketone	9.22	.285	.577

* Relative values for interaction coefficient based on this study.

** An independent determination reported by Dr. A.M. Bueche at the Gordon Conferences, New London, N.H. August 1953 was 0.465 for toluene. This was determined from light scattering measurements in toluene.

controllable factors which affect the magnitude of swell of a specific polymethyldisiloxane elastomer. These factors are related to the amount of cross-links of the vulcanizing agent used in the compound formulation and to the temperature conditions of vulcanization.

More specifically, the degree of swell is dependent upon the solvent and also upon the molecular network of a polymer, whose most significant factor is the molecular weight of the chain between cross-links, called M_c . It was possible to determine M_c by using a theoretical equation derived by P. J. Flory which relates M_c to the degree of swell and to a polymer-solvent interaction coefficient χ , independent of M_c . A special apparatus was constructed to make possible frequent and accurate measurements of sample swells in various solvents. The table on the opposite page shows the equilibrium reached with various fluids. The cohesive energy density of the rubber lies close to the value of the solubility parameter of the solvent or solvents causing the most swelling (Gee). A more accurate method of determining χ is possible if more uniform molecular weight polymer is taken initially.

These swelling tests with various solvents made calculation of cohesive energy density of polymethyldisiloxane elastomer possible. It is equal to $7.50(\text{cal./c.c.})^{\frac{1}{2}}$, which was arrived at by the method of Gee and by a more accurate method proposed by Hauser. The polymer-solvent interaction

coefficients (μ) were shown to be in fair agreement with the theories relating to the heat of mixing the liquids.

The amount of cross-linking agent used in the vulcanization of silicone elastomer was found to vary significantly but not quantitatively the resulting M_c . Varied time and temperature conditions of vulcanization also affected this factor.

TABLE XLI
VARIATION OF M_c WITH THE METHOD OF PREPARATION
OF SILICONE RUBBER

% B.P.	<u>Press Cure</u>		<u>Oven Cure</u>		M_c
	<u>Time, min.</u>	<u>Temp., °F.</u>	<u>Time, hrs.</u>	<u>Temp., °F.</u>	
0.5	15	250	24	300	>24,000
2.0	15	250	24	300	11,000
8.0	15	250	24	300	9,000
2.0	10	250	24	300	17,000
2.0	10	230	24	300	14,000
2.0	15	230	24	300	18,000
2.0	15	250	24	300	11,000
2.0	15	250	1	300	24,000
2.0	15	250	48-hr. cycle to 480°F.		13,000

The values of M_c show that the first two percent of benzoyl peroxide added to a silicone recipe is far more efficient in its cross-linking action than the next six percent.

The rate of extraction of polymer was considered in conjunction with the rate of swelling, and the rate equations were calculated for both processes which seemed to proceed

ad infinitum. The aim of this part of the study was to determine rates of extraction from various samples of silicone rubber and determine if extraction results from the presence of nonvulcanized molecules or from network breakdown during swelling. It was found that the extraction of silicone polymer when it is swollen by benzene may be partly due to solvation of nonvulcanized molecules but it is also partly due to breakdown of the cross-linked network.

DISCUSSION

During the four-year period covered by the two contracts under which this work was done, silicone rubber and its technology have come a long way. Not a little of this progress has been aided by work done under these contracts.

Prior to 1950, knowledge of silicone rubber was rather closely guarded by the suppliers who frankly admitted that this was due to various causes, such as: a) the polymer was inherently a low-tensile polymer and the less publicity, the better; b) the competition between suppliers made publication inadvisable; c) there was a scarcity of compounding information but considerable knowledge of electrical properties; and d) the compounding techniques were so unconventional that they might retard the progress of the polymer if they were publicized. Regardless of the merits of these arguments, the faith in this polymer of the two contracting parties appears now to have been justified.

Silicone rubber is now entering an accelerating growth period in which the improved tensile strength, abrasion resistance, tear resistance and compression set resistance will greatly aid in spreading its use. Publication of compounding data and recipes will bring many more rubber compounders into the field, and progress toward even better products will be rapid. This fact alone

would seem to justify the expense of the work.

It is very definitely true that dimethyl silicone rubber requires more reinforcement than other common synthetic rubbers. The polymer chains appear to be less interlocked mechanically or by van de Waal's forces or by forces of crystallization than those of any other common polymer. However, this fact and the fact that free rotation exists down to a very low temperature account for the greatly superior low-temperature properties of the silicones. It now appears that finely divided pigments, such as Alon and GS199S Silica, are so well wet by the rubber that they permit high elongations to be reached when the rubber is vulcanized. The attractive forces between these (and several other fillers) and the silicone rubber are far greater than those between the polymer chains themselves. It would seem that even greater strengths than those already reached are quite logically to be expected.

Aside from the interest which is rapidly developing in silicone rubber on the basis of improved physical properties, there is a definite possibility that some chemical modification of the fully polymerized silicone rubber may yet be possible to make derivatives which will also be useful. One of these, called G-2, has been made and used in the factory of the contractor for the purpose of lubricating and bonding silicone rubber to the fibers

of glass cloth where the composite is to be used in diaphragms. Such diaphragms, which formerly failed to pass a flexing specification calling for 100,000 flexes, have been meeting this specification without difficulty since the use of the glycerol-stabilized liquid silicone rubber has been introduced. Time has not permitted finding an explanation or mechanism for the improvement. It is, of course, possible that a similar result could be achieved in some cheaper way.

Results being obtained under another contract (NOas 51-766-c), which were predicted by work done on the chlorination of depolymerized silicone rubber under this contract, give promise of improved fuel-resistant silicone rubbers which retain resilience at low temperatures. This goal, which is being sought by all branches of the armed services, if reached, would in itself certainly justify the time and effort spent on it to date.

An intangible but still worth-while result of the two contracts with the Office of The Quartermaster General is the not inconsiderable amount of knowledge of the chemical properties, the compounding know-how, the difficulties and the advantages of silicone rubber which have been studied and reported in this series of fourteen reports. Such information is not available elsewhere, due to the paucity of publication in this new field.

At least one major contribution of a theoretical

nature has been made in the studies of the mechanism of swelling of silicone rubber and how swelling is affected by state of cure. An exact figure for the cohesive energy density of silicone rubber was found. (This has since been confirmed according to a private communication from another laboratory.) The methods and principles of swelling of a vulcanized rubber such as silicone can be used as a tool in further investigations of the mechanism of reinforcement. It is to be hoped that this work can be continued at an early date. The advantages of studying both the theory of reinforcement of rubbery polymers and also the theory of vulcanization of rubber in a system which is as simple as the dimethylsiloxane rubbers are obvious. Here, with a single vulcanizing agent, benzoyl peroxide, and starting with a pure polymer, some of the complicated effects of particle size, particle shape, and the nature of the surface of the particle can be studied and the thermodynamic equations can be worked out for reinforcement. It should also be possible to work out more accurate expressions than heretofore obtained for the stress-strain curves. It would be interesting, too, to investigate the effect of vulcanizing agents other than benzoyl peroxide on the swelling characteristics of the rubber. The number of cross-links produced by benzoyl peroxide is less than that expected on the basis of theory, and the way is open for the development of a

more efficient vulcanizing agent.

Adequate reinforcement of silicone rubber appears to be obtained only when thorough wetting of the filler by the rubber is attained. Several ways of improving this have been found:

1. Dispersion of filler in solutions of depolymerized rubber
2. Prolonged milling
3. Use of fillers which are easily wet by silicone rubber, such as silica, alumina, silica aerogels and certain diatomaceous earths
4. Use of preheating treatments to promote contact between filler and rubber
5. Use of aging and remilling for the same purpose
6. Application of liquid siloxanes to the surface of porous fillers

When any of these methods results in good wetting, and when the filler is of small particle size (0.01 to 0.02 microns), maximum reinforcement results. This usually occurs at 15 to 25 percent volume loading. The cross section of the siloxane chains (40 \AA^2) is still small compared to the cross section of a 0.01μ particle. The latter is $2500 \pi \text{ \AA}^2$. A filler particle of 0.001μ diameter would have a cross section of $25 \pi \text{ \AA}^2$ and would be of the same order of magnitude as the siloxane chains themselves. If this were an easily wetted material,

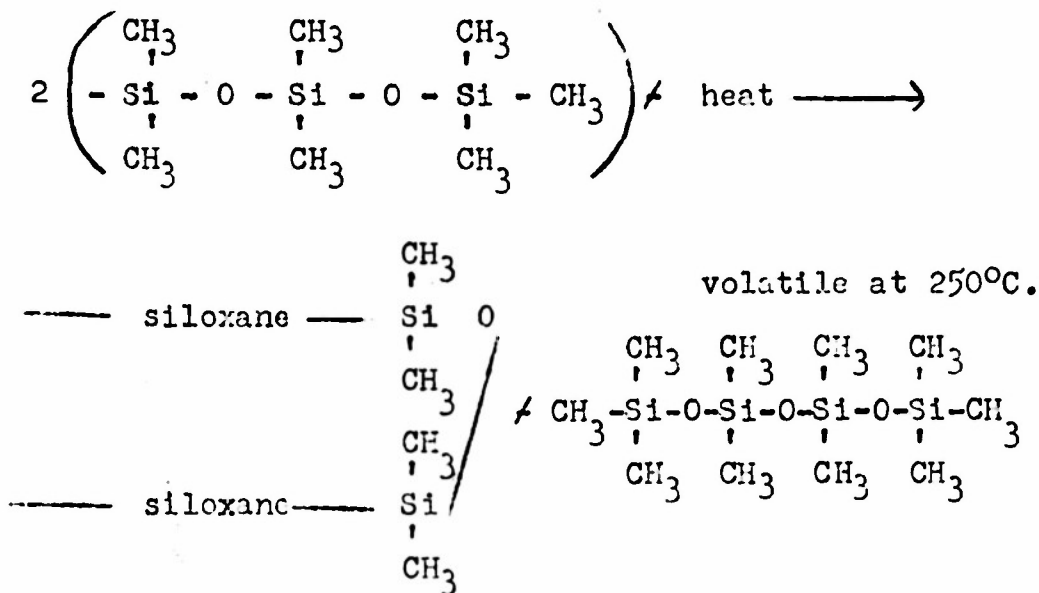
great improvement in reinforcement should result.

Improved tear-resistance seems to result when both tensile strength and elongation at break are high. This appears to occur when reinforcement is not too great, so that strain does not cause localized stresses. The resistance is also improved when fibrous materials are introduced to dissipate localized forces at the tearing centers.

High elongation occurs when peroxide concentrations are low or when fillers such as Alon or titanium dioxide interfere with normal action of the benzoyl peroxide. Control of the curing action of GS199S Silica by limiting the time and temperature of curing or aging also results in high tear-resistance. High-molecular-weight silicone rubbers which require fewer cross-links to vulcanize them should have outstanding tear-resistance.

It has been observed in this work that reduced benzoyl peroxide generally results in some improvement in compression set resistance. This appears to be due to reduced depolymerization in the presence of less benzoic acid. The effect is small but definite, as is the improvement resulting from lowered curing temperatures (press curing) and for a similar reason. Long oven cures are evidently needed to shake loose and evaporate low-molecular fragments which might otherwise break loose during the compression set determination, thus causing cross-links to form during the test with a resultant high set. It is

assumed, here, that cross-links are formed when chain ends break loose.



If such reactions occur during oven cure, they would not change greatly the value of M_c as has been found to be true, but they might greatly reduce ultimate elongation, as is also true, and they should definitely reduce the formation of cross-links during compression set determinations.

Preheating, as practiced here, should reduce compression set, as was found to be the case.

A prediction of the future of Alon and GS199S Silica insofar as they are related to silicone rubber may not be out of place. Both fillers face tough competition because they are expected to cost at least a dollar per pound in comparison with Santocel C and Aerosil at prices

less than a dollar per pound. This would be especially true if silicone rubber eventually reaches a "popular price" of a dollar per pound. For those applications where outstanding tensile strength and elongation, abrasion- and tear-resistance are needed, and many more such applications will be found in the future, GS199S Silica will be required until improved types of this or other fillers make it obsolete. The technical public will not be satisfied permanently with a rubber which is strong only when reinforced with glass fabric. There is an excellent chance, also, that use will be made of the resinous properties imparted at high curing temperatures by GS199S. Flexible resin coatings can be made from silicone rubber and GS199S Silica. We have, as yet, no knowledge of the relative value of these versus the commercially available silicone resins.

The study, here, of the mechanism of peroxide vulcanization is not considered as completed research. We still do not know with sufficient accuracy the disposition of all the peroxide. We know only that a considerable portion of it is wasted, particularly if high concentrations are used. This subject needs further study, and better cross-linking agents are needed.

The question of molecular weight should not be considered one to be answered with convenience for the manufacturers of silicones. While it may be true that

the heterogeneous polymers of the past require such strong reinforcement that one must necessarily use a rubber containing much lower polymer in order that it may be milled, extruded and calendered, it is to be hoped that greater chain length may reduce the amount of reinforcing filler needed and thus make it possible to use a less "soupy" polymer. Polymer or resin at \$4.00 per pound is much too expensive an item to evaporate in a curing oven. It has been clearly shown that the higher molecular weight polymer is to be preferred when GS199S Silica is the reinforcing and curing agent. Benzoyl peroxide, however, tends to cover up the defects of low-molecular-weight silicone rubber.

At this time, no important application of the relatively easy depolymerization of silicone rubbers with acids or acidic substances, other than reclaiming, is foreseen. As a method of producing a soluble siloxane material for further reactions, it would seem that better reactants could be made directly from the monomers. As a possible method for producing reactive surfaces against which other materials may be bonded, it would seem that there are some possibilities. Some work, using such techniques, has been carried out under contract with the Department of the Navy (NOas 51-766-c).

This discussion would not be complete without suggestions or recommendations to the Government concerning

further research and development work on the silicones.

(1) It is advisable that the Office of the Quartermaster General continue to maintain contact with an industrial concern which is interested in making articles out of silicone rubber, so as to take advantage of the latest improvements in the field, whether they may stem from the work recorded here or from unsponsored developments.

Such contact does exist between the Office of the Quartermaster General and The Connecticut Hard Rubber Company (DA 44-109-qm-1246). Products on which development work is being carried out include V-belts made from silicone rubber, heat-resistant flue patches for tents, and electrical connectors made from silicone rubber wire. Independently, the Connecticut Hard Rubber Company has fabricated a retread compound using silicone rubber reinforced with GS199S silica and has shown in road tests that its abrasion resistance is of a quality comparable to that of standard retread materials.

(2) We recommend that fundamental research be sponsored by the Government through one of its defense agencies to study further mechanisms of reinforcement and also to study the mechanism of vulcanization of silicone rubber. This Company would be interested in carrying out such research because it feels that continued fundamental research is essential to provide data which later result in better raw materials out of which improved products

are produced. We submit that the history of the whole polymer field is a demonstration of this point.

It is also recommended that a program in a competent laboratory be sponsored for the purpose of fitting stress-strain curve equations to the stress-strain curve of the silicone rubber. The simplicity of recipes for vulcanizing and reinforcing silicone rubber and the possibility of producing relatively uniform molecular weight fractions of the rubber should give rise to very accurate data in a problem of this kind. Furthermore, the freedom from harmful degradation by oxygen and the wide temperature range over which the polymer is completely stable would make it possible to carry out such research over a wide temperature range and permit determination of the effect of the temperature parameter. Contracts of this type have the advantage in that they provide not only the fundamental research but trained investigators.

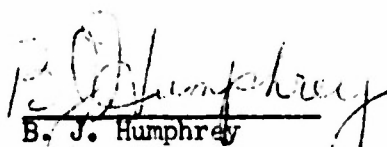
(3) Stronger, more useful silicone rubber appears to be possible (a) by producing higher molecular weight rubber, and (b) by producing even finer filler particles with which to reinforce it. Such systems will undoubtedly be produced eventually. They could be produced, at least experimentally, more rapidly if research and development work were sponsored by the Government. It is recommended that if funds are available, and if a satisfactory program can be obtained from an industrial firm such a contract should now be initiated.

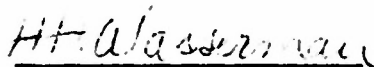
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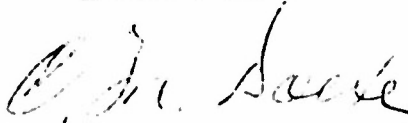
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